

HIGH TEMPERATURE STEAMING FOR DYE FIXATION
IN POLYESTER-COTTON BLENDS

A THESIS

Presented to

The Faculty of the Division of Graduate Studies

by

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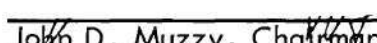
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HIGH TEMPERATURE STEAMING FOR DYE FIXATION
IN POLYESTER-COTTON BLENDS

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TABLE OF CONTENTS

| | Page |
|-------------------------------------|------|
| ACKNOWLEDGMENTS | ii |
| LIST OF TABLES | vi |
| LIST OF ILLUSTRATIONS | vii |
| SUMMARY | x |
| Chapter | |
| I. INTRODUCTION | 1 |
| Purpose | |
| Background | |
| Scope and Limitations | |
| II. LITERATURE SEARCH | 10 |
| Cotton | |
| Polyester | |
| Polyester-Cotton Blend | |
| An Introduction to Dyeing | |
| Disperse Dyes | |
| Reactive Dyes | |
| Dyeing Cotton with Reactive Dyes | |
| Dyeing Polyester with Disperse Dyes | |
| Dyeing Polyester-Cotton Blends | |
| Migration | |
| Dyeing Auxiliaries | |
| Thickeners | |
| Urea | |
| Carriers | |
| Surfactants | |
| Dispersing Agents | |
| Thermofixation | |
| Mechanism | |
| Urea | |
| Disperse Dyes | |

| | | |
|------|---|----|
| | Reactive Dyes | |
| | Polyester | |
| | Cotton | |
| | Advantages of HT-Steaming | |
| | Equipment | |
| III. | EXPERIMENT DESIGN | 72 |
| | Introduction | |
| | Yarns Structure and Specifications | |
| | Yarns Preparation for Dyeing | |
| | Padding Liquor Formulation | |
| | Equipment Design | |
| | Boiler | |
| | Superheater | |
| | Steamer | |
| | Temperature Control and Measurement | |
| | Padder and Residence Time Control | |
| | Yarns Take-Up | |
| | Yarns Driving | |
| | Start Up | |
| | Shutdown | |
| | Sampling of Yarns | |
| | Washing Off the Unfixed Dye | |
| | Disperse Dye | |
| | Reactive Dye | |
| | Disperse and Reactive Dyes | |
| | Disperse Dye Extraction | |
| | Dye Concentration Measurement | |
| IV. | RESULTS AND DISCUSSIONS. | 98 |
| | Steaming Temperature Effects on Polyester Fibers | |
| | Introduction | |
| | Microscopic Analysis of the Ruptured Yarns | |
| | Tensioning Weight Variation | |
| | Steaming Residence Time Reduction | |
| | Polyester Fibers Melting Point Determination Using the Hot Plate- | |
| | Method | |
| | HT-Steaming Heat Transfer Mechanism | |
| | Further Experiments on Polyester Melting | |
| | Polyester Melting Dependence on Steaming Temperature | |
| | Critical Operating Conditions | |
| | Polymers Heterogeneity | |

| | Page |
|--|------|
| Polyester Fibers Melting Point in HT-Steaming | |
| Steam Mass Flow Rate Effect on Polyester | |
| Higher Temperature Steaming Effects on the Polyester Yarn Tenacity | |
| Residence Time Effect on Dye Fixation | |
| General | |
| Disperse Dye Fixation Yield | |
| Extended Steaming Exposure Effect on the Fixed Disperse Dye | |
| PH Effect on the Disperse Dye Fixation | |
| The Reactive Dye Interference with the Disperse Dye | |
| Dyes Entrainment | |
| Fiber Swelling | |
| V. CONCLUSIONS AND RECOMMENDATIONS | 127 |
| Conclusions | |
| Recommendations | |
| APPENDIX | |
| A. INTRODUCTION | 131 |
| B. LITERATURE SEARCH | 137 |
| C. EXPERIMENT DESIGN | 141 |
| D. RESULTS OF EXPERIMENTS | 160 |
| BIBLIOGRAPHY | 183 |

LIST OF TABLES

| Table | | Page |
|-------|--|------|
| 1. | Historical Development of Synthetic Dyes | 132 |
| 2. | Regenerated Man-Made Fibers | 134 |
| 3. | Synthetic Man-Made Fibers. | 134 |
| 4. | Fibers Dyeing | 136 |
| 5. | Physical and Mechanical Properties of Cotton and Polyester Fibers | 138 |
| 6. | Complementary Properties of Cotton and Polyester. | 140 |
| 7. | Light Absorption of Disperse Dye Solutions | 157 |
| 8. | Light Absorption of Reactive Dye Solutions | 158 |
| 9. | Light Absorption and Dye Concentration in Solutions | 159 |
| 10. | HT-Steam Disperse Dye Fixation | 179 |
| 11. | Disperse Dye Fixation Yield | 180 |
| 12. | Polyester Fiber Disperse Dye Fixation in the Polyester Yarn and Blended Yarn. | 181 |
| 13. | Condensed Steam Solution and Simulated Dye Solution Spectra | 182 |

LIST OF ILLUSTRATIONS

| Figure | | Page |
|--------|---|------|
| 1. | Boiler | 142 |
| 2. | Sketch of the Electric Heating System | 143 |
| 3. | Temperature Control Electrical Diagram | 144 |
| 4. | Steamer | 145 |
| 5. | Padder and Take-Up Systems. | 146 |
| 6. | The Thermometer Calibration | 147 |
| 7. | Yarns Driving. | 148 |
| 8. | Guiding Pulleys | 149 |
| 9. | Pending Weight from Tensioning Pulley | 150 |
| 10. | Tension Force Distribution on the Driven Yarn | 151 |
| 11. | Yarn Holder. | 152 |
| 12. | Spectra of Dyes Dissolved in DMF Solutions at Different Concentrations | 153 |
| 13. | Spectra of Disperse Dye Dissolved in Water at Different Concentrations | 154 |
| 14. | Spectra of Reactive Dye Dissolved in Water at Different Concentrations | 155 |
| 15. | Relation between Dye Concentration and Light Absorption | 156 |
| 16. | (a) Untreated Yarns | 161 |
| | (b) Untreated Polyester Fibers. | 161 |

| Figure | | Page |
|--------|--|------|
| 17. | General View of HT-Steamed Yarns at 220 deg. C | 162 |
| 18. | Polyester Fiber Fusion in a Polyester Yarn that has been HT-Steamed at 220 deg. C | 163 |
| 19. | Polyester Fiber Fusion in the Polyester Yarn Due to Steaming at 220 deg. C | 164 |
| 20. | Polyester Fiber Fusion in the Polyester-Cotton Blended Yarn Due to Steaming at 220 deg. C | 165 |
| 21. | (a) General View of Polyester Yarn Broken Ends Due to HT-Steaming at 220 deg. C | 166 |
| | (b) Polyester Fiber Partial Melting at the Yarn Periphery. | 166 |
| 22. | The Polyester Fiber Partial Melting at the Yarn Periphery. | 167 |
| 23. | (a) Neck Formation in the Polyester Yarn Caused by HT-Steaming at 220 deg. C and Comparison to an Untreated Yarn | 168 |
| | (b) Neck Cross Sectional View and Polyester Fibers in the Yarn Cavities | 168 |
| 24. | Neck Cross Sectional View | 169 |
| 25. | (a) Cotton Fibers prior to HT-Steaming | 170 |
| | (b) HT-Steamed Cotton Fibers | 170 |
| 26. | (a) Untreated Cotton Fibers. | 171 |
| | (b) Steamed Cotton Fibers. | 171 |
| 27. | The Disperse Dye Thermofixation Data | 172 |
| 28. | Untreated Polyester Yarn Load-Elongation Curve. | 173 |
| 29. | HT-Steamed Polyester Yarn Load-Elongation Curve. | 174 |
| 30. | HT-Steaming Disperse Dye Fixation. | 175 |
| 31. | HT-Steaming Disperse Dye Fixation Yield | 176 |

| Figure | | Page |
|--------|--|------|
| 32. | Polyester Fiber Disperse Dye Fixation in the Polyester Yarn and Blended Yarn | 177 |
| 33. | Condensed Steam Solution and Simulated Dye Solution Spectra | 178 |

SUMMARY

Polyester-cotton blends have become increasingly popular in the apparel and household industry; their functional and aesthetic qualities imparted have been recognized by both designers and consumers. Dyers in particular are faced with the responsibility of dyeing this blend economically, without sacrificing its distinguishing features that are paramount to the modern consumer.

The objective of this research work is to investigate a continuous process for the dyeing of polyester-cotton blended yarns in a simple sequence of operations that starts by padding the dyeing liquor onto the cleansed yarns; then steaming for the purpose of heat-setting, drying, and fixing the dyes into the yarns. This is then followed by washing and drying the yarns.

The steaming unit and its operating conditions have been the major concern to the author. Superheated steam--practically at atmospheric pressure--has been utilized. The design of the steamer is such that steam is released out of the equipment at a slightly higher pressure than atmospheric; in order to prevent air from entering the unit. The variation of the most influential operating conditions, i.e., temperature and residence time, have been investigated to study their interaction and influence on the extent of dye fixation in an attempt to determine the most favourable mode of operation for the particular dye-fiber systems examined.

Three yarns of similar structure, i.e., count, twist per inch, and average staple length, but of the following composition: 100% polyester, 100% cotton, and 50%-50% polyester-cotton blend, have been dyed simultaneously with three different dyeing systems, namely, disperse, reactive, and disperse-reactive dyes.

The conclusion is that time, energy, and effort can be minimized during the continuous dyeing of polyester-cotton blends by the use of the pad-HTsteaming process without separate heat-setting and intermediate drying by utilizing superheated steam at the appropriate temperature and during a suitable period of time. A typical steaming is carried out at 200 deg. C for a period of one minute.

Furthermore, it has been found that the superheated steam causes a considerable drop in the melting point of polyester. In addition, at steaming temperatures as high as 220 deg. C a remarkable reduction in the mechanical properties of the polyester has been noticed--suggesting a possibility of hydrolysis. On the other hand, a significant amount of the disperse dye and reactive dye is entrained with the steam leaving the equipment to the surrounding atmosphere.

CHAPTER I

INTRODUCTION

Purpose

Chemical Engineering is simply concerned with unit operations and unit processes. The former are basically operations for handling of fluids and solids, heat generation and transfer, diffusional operations, and multiphase contacting and separation. The latter are processes involving chemical reactions.

It took the chemical industry about a generation to make full use of chemical engineers but apparently it is going to take much more before the textile processing industry makes similar proportional use of these engineers (30). These comments were stimulated by a paper published in 1948 that, interestingly enough, includes remarks that are once more valid today:

Chemical Engineering in the textile industry presents a puzzle. Why, when there is so much for them to do are there so few chemical engineers in bleaching and dyeing? We see an industry that has known hard times and may know them again. During the prosperous times the general philosophy was to get while the getting's good and no nonsense about plowing back.... The textile industry is steeped in the tradition of craftsmanship.... The Master Dyer for instance is a man of distinction. His art and his little black book rule the dye house.... When the bottom dropped out... the industry was caught with old methods and no reserves. Competition became cut throat, lots of mills went under and the rest not far from it.... He'll (the chemical engineer) find no golden opportunity in a marginal mill, flush while the boom lasts and flat when it's over; nor in a newly rich mill, flirting lavishly with science to impress the stockholders, but never really intending to marry the girl, nor in a mill where the

owners, in spite of the twenties, still figure a fast dollar in the hand is worth two over the long haul (20).

Sizing, scouring, bleaching, mercerising, heat-setting, padding, drying, dyeing, steaming, washing, finishing, etc., are essentially chemical engineering problems. However, it is doubtful that dyeing, for instance, has been considered a unit process or taught as such; instead, dyeing has been regarded as a craft.

The engineering principles may provide possibilities for improving dyeing process design, consumption of dyestuffs, and enhancing reproducibility when required. The wet textile industry has been slowly developing, while many other chemical industries are functioning more effectively and operating, comparatively, with a minimum of waste, expense, and unnecessary effort. Accordingly, the exploration of major processes in the textile industry, like dyeing, is a necessity for more development and efficacious utilization of available resources and human effort.

Unfortunately, dyes have not been sufficiently standardized. A dye of a well defined chemical structure might be produced by ten manufacturers, but without any specifications of either the purity, the nature of impurities, or any other ingredients present, e.g. dispersing agents, surfactants, buffers. The same rule applies to auxiliaries, e.g. thickeners, wetting agents, carriers, dyeing retarders. Therefore, any research work for the purpose of rationalizing a general technique for dyeing a specific fiber becomes difficult and complex, unless the dyes and auxiliaries used are purified--a process that would not necessarily simulate the behavior of commercial dyestuffs. Furthermore, fibers also have their own problems of standardization.

The purpose of this research is essentially to investigate the possibility of dyeing polyester-cotton yarns in a simple and rational sequence of operations as follows: padding simultaneously the disperse and reactive dyes onto the yarns; then, fixing the dyes into the fibers with superheated steam at high temperature and under effectively atmospheric pressure. No intermediate drying is performed, thereby, minimizing the dye migration problem, saving energy, and sparing more space in the crowded dye houses. Furthermore, the fixation of the low energy dyes with high temperature steam (HT-steam), by comparison, results in a remarkable reduction in the common auxiliaries used during the dyeing of this blend, causing a decrease in operating expenses. In addition, less urea is necessary during the HT-steaming process, resulting in less contamination of the equipment as well as a decrease in pollution.

It is an objective of this work to whet the appetite of chemical engineers for further exploration of this challenging and colorful world of dyeing. However, the ultimate purpose of this research is the common one for any scientific investigation, that is, an attempt to answer questions regarding the understanding and control of the observed phenomena via isolating the latter and closely examining the interactions involved. Subsequently, the observations are analysed to either answer some of the questions, or raise some more.

Background

Coloring is one of the oldest arts conceived by the human being. The prehistoric man first tried coloring different objects before deciding to dye his

apparel; then, imparting colors on his body. Needless to say that the prehistoric woman was doing probably more than just watching this interesting progress taking place. The earliest sources for pigments and dyes were vegetables as well as animals. Ancient Egyptian hieroglyphs contain a thorough description of the extraction of natural dyes and their application in dyeing.

Using the sense of sight for combining colors constitutes a language for transmitting feelings in instances where words with their limited logic become impotent and sterile. The usage of colors is indispensable for the individual to express himself in the community; and like a language, the process of choosing a color and arranging it in a sentence among others is the resultant of the past history of the individual. A normal person does not remain inert at the sight of colors; they always generate in him responses of varying degrees of intensity. This is why color is basically a psychophysical effect.

One of our most intimate fields of color action is cloth. A man who wants to look sober would not wear a wide-striped white and red pair of pants; although a woman would be more colorful--a behavior resulting from her relatively different psychological structure. On the other hand, persons belonging to some civilian, military, police, and similar agencies are required to disregard their individualism by a uniform, which is basically a unified colored dress to identify those who wear it as members of a specific group.

Therefore, the ultimate function of dyeing is to vitalize some of our special and growing feelings--particularly in the modern society--as well as the need

for colored cloth to shelter against monotonous stresses that can strongly influence the performance of an individual.

Apparently because of the continuously varying production in dye houses; no sufficient care has been taken to standardize the different products involved for efficacious reproducibility. It was only when natural sources for dyes manufacture became scarce that first attempts for dye synthesis were made. In 1771, Woulfe succeeded in producing picric acid, which was used occasionally for dyeing silk yellow (93). This attempt was followed by a similar one in 1834, when Runge discovered resolic acid (76). However, the industrial production of dyes did not initiate before 1856, when W. H. Perkin produced a violet cationic dye that he called Mauveine and developed a process that was commercialy feasible for the dye manufacture from coal tar (93); thereafter, dyes came more quickly as can be shown from Table 1 in Appendix A.

Natural fibers had been the basic constituents of fabrics, belts, cords, etc., for a wide variety of applications. The increasing demand on textile fibers as well as the need for new fibers having different properties led to the conception of man-made fibers. A brief review of the historical development of man-made fibers is shown in Tables 2 and 3 in Appendix A. Table 4 includes a general review of the dyeing behavior of different fibers with various dyes.

No revolutionary progress had been made in the dyeing processes until 1948, with the development of the molten metal dyeing machine in Germany by D. Benediktov (10). At the same time a totally independent research work in the

field of molten metals was in progress in England by The Standfast Dyers and Printers of Lancaster (14). This research led to a series of new vat dyes destined to be used with the Standfast machine; among these was the well-known vat color Jade-Green (83). The Standfast machine was not used until the late fifties for commercially dyeing cotton with vat dyes. It is interesting to note that in 1903, a British patent was granted to Mather and Hepbern for the use of mercury as a medium for heating fabrics in bleaching and other processes (89). Other novel machines embodying new principles are the compressive-shrinkage machine (the Bradford Dyers Association and Cluett-Peabody) and the micro-stretch machine (Raduner) (30).

The development of continuous processes for the dyeing of polyester-cotton blends started in the early fifties; with the research work lead by the Dupont Company to introduce the Thermosol process. This process makes use of hot dry air as a fixing medium at temperatures as high as 200 deg. C and exposure times of a few minutes, e.g. 2 min for good dye fixation (44). The thermosol process was particularly successful in the U.S.A. and started to be used commercially in the late fifties. The process required new dyes of higher heat fastness and low activity (55).

A more recent process is the HT-steaming developed in the mid-sixties by the Imperial Chemical Industries (ICI). This process makes use of superheated steam at atmospheric pressure for dye fixation (69, 39). It became very popular for the dyeing of polyester-cotton blends. Reactive and disperse dyes of higher

heat fastness and lower activities also had to be developed, e.g. Procion H and Dispersol (both produced by the ICI). A typical dye bath composition for the dyeing of polyester-cotton blend is as follows: disperse dye, x g/l.; reactive dye, y g/l.; urea, from 0. g/l. to 164. g/l.; sodium bicarbonate, from 8.2 g/l. to 15.8 g/l. Anionic surface active agents and thickeners can be dispensed with as well as urea. Thus, a great reduction in the consumption of auxiliaries is possible by the use of the HT-steaming process. This progress was made due to more understanding of the chemistry, physics, and chemical engineering of dyeing (39).

Scope and Limitations

The scope of this work focuses on the rational of dyeing processes. Starting with a well defined fiber structure and aiming towards a specific color of given fastness properties suiting a certain end use would be enough for an efficient dyeing process design. This first necessitates the understanding of the dyeing phenomena with the major physical and chemical interactions involved; thereupon, the use of chemical engineering principles for the design becomes possible.

Considerable work has been done in exploring the dyeing theory; but still, much more has to be done before making use of the full potential of these theories in the textile industry. Chemical engineers have the potential for applying these theories in the industrial field because of their close concern to problems related to heat and mass transfer either with, or without chemical reactions.

Some limitations are opposing the application of engineering principles to dyeing processes; lack of standardization in the dyestuffs and fibers, secrecy, and

fragmentary research work are major problems to be solved.

Identification of dyestuffs in the market is made by the brand name followed by the hue of the dye, then a series of letters and numbers. This is like the early days of this century in the chemical industry when oil of vitriol (sulfuric acid), green vitriol (ferrous sulfates), and aqua fortis (nitric acid), etc., were used for designating basic chemicals. Interestingly enough the purity of commercial dyes is in the order of magnitude of 20%; the rest of it might be dispersing agents, anionic surfactants, dyeing retarders, etc., and sometimes sugar (18). A similar identification system is adopted for fibers.

These factors result in supplementary efforts and expenses each time a new fiber-dye combination is processed in order to determine the appropriate conditions for operating various dyeing equipment in different dye houses. Dyeing instructions provided by the dye manufacturer are obtained from experiments on laboratory equipment that might not simulate the behavior of various full scale industrial dyeing machines.

It would be advantageous to identify dyes by the chemical structure of the different species present, as in the chemical industry, in addition to the Color Index number (C.I. number) as an indication to the dyer of fastness properties and applicability to fibers. Dye additives should be kept at a minimum; and it would be more desirable if the dyer adds these components by himself when necessary. This would be enhanced by more coordination between the dyer and the dye manufacturer. On the other hand, a similar system can be worked out for

fibers and other auxiliaries.

Secrecy and research work administration are everyday problems; extensive studies have been made in this area. This is how E. Wilson conceives such problematic matters:

The greatest difficulties, and consequently the greatest losses in efficiency, occur when secrecy, either military or industrial, is involved.... Admittedly secrecy is sometimes necessary, but less often than believed.... Another problem facing the research director is how to divide his resources between direct attacks on immediate problems and longer range fundamental studies.... So often the immediate problems appear to be very urgent that long range work is disrupted. Everyone with wartime or industrial experience knows that in a large fraction of the cases the urgency disappears or eclipses by a newer emergency before the first problem is solved. This is clear proof that insufficient thought was given to the original statement of the problem (114).

More specifically in the field of color recipe formation for dyeing; the following comment was made during the 1973, meeting of the Color Association:

Another difficulty confronting anybody engaged with the practical aspects of color recipe formation is the still comparatively dense veil of secrecy over the whole subject.... Fortunately this veil is gradually lifting as a result of the recent publications by industry offering genuine know-how. This is to the advantage of the young science which can only benefit by such give and take (42).

Basic research and coordination arranged so that information acquired by one group is available to others who need it, are strongly recommended to increase the efficiency of research work and accelerate progress in the dyeing industry.

CHAPTER II

LITERATURE SEARCH

Cotton

Cotton is the oldest and the most important of the textile fibers. An interesting comment has been made by Moncrieff in his book entitled, Man-Made Fibres, about cotton:

Cotton is a wonderful fiber, and it will be a long time before the best of our polynosic rayons can equal it. The basic objection to cotton growing is that it needs a lot of labour; people are not overfond of work and have to be paid highly to do it. Cotton is therefore an expensive crop to pick (76).

Cotton grows in warm climates; it grows on bushes, three to four feet high. The blossom appears in June; as it withers, it is succeeded by a closed pod. The latter contains seeds from which the fibers actively grow. When the seeds are nearly ripe the pod bursts open and the cotton hairs stand out forming a white fluffy mass. This is called a boll. The fibers are now exposed to the sun completing their ripening; the contents of the cell gradually dry up producing one of the characteristic properties of cotton, namely, its twist. Cotton is usually ripe for gathering between August and October (103).

After the crop has been gathered, the fibers are removed from the seed by the ginning process, then, they are tightly packed in bales weighing about 500 lb. each. Complete mechanization and chemical weed control have reduced

the number of man-hours required to produce one bale of cotton from 155 hr to 12 hr. The bales arriving at the spinning mill vary considerably in uniformity and quality; therefore, it is necessary to blend together a number of bales to insure a uniform product. It all starts in the opening machine that loosens and fluffs the fibers ten to fifteen times as bulky as it was in the bale. The fluffy cotton is then fed to the picking machine, which cleans the fibers from fragments of seed coat, portions of leaf and stem, and accidental dirt; in addition, it continues the loosening of the fibers and forms them into a continuous sheet called lap. The fiber lap is then supplied to the carding machine, which straightens the fibers and forms them into a thin filmy sheet. This sheet is then brought together as a soft rope called card sliver. Several slivers are then blended together by the drawing frame which also parallels the fibers. This is simply done by driving the slivers through sets of rolls, each running successively faster than the preceding set. Roving is the last step before spinning; its purpose is to draw out the sliver to a size suitable for spinning, increase the parallelism of the fibers, and improve the yarn uniformity by drawing two or more slivers together. A roving is a continuous, soft, slightly twisted strand of fibers comparable in size to a thin pencil. Spinning is the final operation in the making of single yarns where simultaneous drawing, twisting, and winding operations take place continuously in a ring-spinning frame (53).

Cotton fibers range in diameter from 16 to 20 microns and in length from three-quarters of an inch to two inches, depending on the variety. Each fiber,

however long or short it may be, consists of one single complete vegetable cell, which is a unicellular hair collected from the seed of the cotton plant. In a young and growing cell, the cellulosic outer skin is filled with the living protoplasm and cell sap so that the structure is distended and turgid. When the cell becomes mature the protoplasm dies and the sap evaporates, leaving an almost empty structure. Deposited salts and protein in the central cavity are amongst the impurities that have to be removed when the cotton is scoured and bleached. Proper drying up of the cell in the sun is a very important factor in producing one of the essential properties of cotton, namely, its characteristic twist (103).

It is possible to discern four principal components of the cotton fiber. A cuticular layer of wax and pectic matter covers the primary wall of the young cell, which becomes the outer skin of the mature fiber. The secondary wall constitutes the bulk of the cellulosic component and is formed of successive layers visible as rings in the cross-section of a swollen fiber which directly correspond with the daily growth of the latter. Finally, there is the lumen, which is the cavity left by the dried protoplasm and cell sap. The lumen has a thin film lining of residual proteinic matter (103).

Cold water causes cotton to swell, but has no chemical action on it; although, the absorption process is exothermic. The swelling of the fiber is accompanied by the disappearance of the natural twist which reappears on drying. Boiling cotton with dilute acids ultimately hydrolyses the cellulose to glucose. At lower temperatures, acids give rise to tendering with the formation of hydro-

cellulose. A common procedure for removing cotton from a polyester-cotton blend is to dissolve the cellulosic component in a 70% sulfuric acid solution at room temperature. Mild alkalis, such as sodium carbonate, have no action on cotton at low temperatures nor at high temperatures in the absence of air. The presence of oxygen in air causes the gradual production of oxycellulose with consequent tendering (103).

Some of the physical and mechanical properties of the cotton fiber are shown in Table 5 Appendix B.

Polyester

Poly(ethylene terephthalate) (PET) is a polymeric ester formed by reacting a dibasic acid and a glycol. The most common monomers used are terephthalic acid and ethylene glycol. However, other monomer combinations are used for commercial synthesis of PET fibers, e.g. terephthalic acid and 1,4-cyclohexanedimethanol, or terephthaloyl chloride and ethylene glycol (70).

The raw material for the monomers is petroleum. Oil is cracked to give ethylene, which is catalytically oxidized with air to ethylene oxide, which is finally hydrated to ethylene glycol. Para-xylene is oxidized to terephthalic acid, which must be free from the meta and ortho isomers. The para-xylene comes from a fraction of the naphtha that is distilled from petroleum (76).

Polyester--used conventionally to designate PET in the textile industry--is a step-growth polymer prepared by the addition-elimination reaction of the carbonyl double bond of a carboxylic acid or a carboxylic acid derivative usu-

ally via direct esterification reactions. The manufacturing steps of PET vary considerably depending on the chosen monomers as well as the reaction conditions (67, 70, 76).

Two impurities are normally present in the polyester fiber. A small part of the ethylene glycol used in the synthesis is converted to diethylene glycol, which can cause a serious drop in the melting point of the polymer. The other undesired impurity is the cyclic trimer that may wash out of the fiber during dyeing, float on the dye bath and reprecipitate on the dyed material (76).

Molten polyester is extruded to produce a continuous filament or a staple fiber. A continuous filament yarn is produced by drawing together the individual filaments emerging out of the spinneret at an average speed of 1000 m/min or higher. This yarn is then fed to draw - twist machines, where it is hot-stretched to about five times its original length. Very coarse filament yarns, owing to their poor thermal conductivity, have to be cold-drawn; fine filament yarns are always hot-drawn. Staple fiber is made in just the same way until the spinning step; during which a great number of filaments are spun and brought together to form a thick tow. The tow is drawn, crimped mechanically, heat-set, and cut into specified lengths suitable for spinning on different systems. Polyester yarn from the staple fiber may be produced by a process similar to the one used for cotton, i.e., opening, carding, drawing, roving, and finally spinning in a ring-spinning frame (53, 76).

Resistance of polyester to weak acids is good even at boiling tempera-

ture and to strong acids it is good in the cold. Weak alkalis have a negligible effect on polyester, while strong alkalis can damage the fiber specially at high temperature. One point to which attention should be drawn is that, because polyester is so readily hydrolysed at high temperature, it is essential to dry the solid polymer before melt spinning is started. Most alcohols, ketones, soaps, detergents, and dry cleaning agents have practically no chemical action on polyester (70, 76).

Table 5 in Appendix B, shows some of the physical and mechanical properties of polyester.

Polyester-Cotton Blend

In 1954 a 65% Dacron 54, 35% cotton blend became a staple item. Comfort properties of polyester were improved by blending it with cotton (53). The outstanding properties of the blend are excellent strength, good washing, easy-care characteristics, high wear resistance, and good wearing properties (102).

A blend of two components yields a material of intermediate values, that is, the predicted value of the blend is lower than the high value of one component by itself, and is greater than the low value of the other component. Actually, the real values do not come out in exactly the same proportion as the respective percentage in the blend (53).

Blending is a complicated and expensive process, but it is done for several reasons:

1. Cross-dyed effects and new color combinations can be obtained, e.g. special color effects are obtained by blending different proportions of stock dyed fibers.
2. Improving spinning, weaving, and finishing efficiency or uniformity of product. This is frequently done with the natural fibers which are never uniform in length or diameter.
3. Better texture, hand, or fabric appearance can result, e.g. fibers with different shrinkage properties are blended to produce bulky and lofty fabrics.
4. Economical reasons, e.g. expensive fibers can be extended by blending them with more plentiful fibers like a blend of cashmere and polyester.
5. Fabrics with better performance are obtained, a good example is the polyester-cotton blend as can be shown from Table 6 in Appendix B.

When the physical properties of two fibers differ, e.g. polyester and cotton, it is not always practical to blend them before carding. The two components are picked and carded separately and then the card slivers are blended on the drawing frame. The problem of mixed wastes is eliminated with this method of blending (53).

In a 50%-50% polyester-cotton blend half the material by weight is cotton, half polyester, however, variations from spot to spot in the yarn and also from inside to outside. Long, fine fibers as polyester tend to move to the center of the yarn, while shorter, coarse fibers as cotton migrate to the periphery of the yarn (3, 53). Therefore, polyester is not visible in proportion to its

weight (96). This phenomenon is referred to as "coring". The same is also true for other polyester-cotton blends.

An Introduction to Dyeing

All dyeing processes entail three different fundamental stages. The dissolution or dispersion of the dye in a medium such that it will be readily absorbed by the fiber under the dyeing conditions. The next stage is the transfer to and adsorption on the surface of the fiber. This is followed by the penetration and diffusion of the dye into the fiber (58). The preferential absorption of the dye from a solution and retention by the fiber is due to electrical, dipole, or hydrophobic interactions as well as the extent of mobility the dye molecule acquires in the system.

Wegmann (110) categorized fixation into four modes according to the nature of the bond between dyes and fibers:

1. Inclusion of molecular or crystal fragments, i.e. mechanical containment, using water-soluble molecules or pigment dispersions.
2. Adsorption of molecules on and in the substrate, i.e. attachment through secondary valence forces.
3. Reaction of dye molecules with accessible and active nucleophilic groups in the substrate to form covalent bonds.
4. Polyreaction of molecules with one another on and within the substrate via polycondensation, polyaddition, or polymerization.

Very frequently, the dye fixation occurs by more than one mechanism.

Furthermore, not all the dye molecules fixed in a fiber have the same dye-fiber bond strength. Reversible adsorption occurs in cases where fixation primarily stems from adsorption of the dye on the hydrated inner surfaces of the fiber through secondary valence forces. This type of fixation gives rise to limited wet fastness properties especially on hydrophilic fibers, e.g. disperse or direct dyes have a modest wetfastness on cotton (37). It has often proved necessary to make the dye capable of further reaction or prone to chemical change to overcome this deficiency. Increasing the molecular size of the colorant, e.g. diazotization and coupling, and removing the solubilizing groups from the dye molecule, e.g. vat dyeing, are well established methods to strengthen the initial dye-fiber association.

Drost-Hansen (29) investigated the role of water structure near solid interfaces. Evidence is presented for the existence of ordered water structure elements near aqueous-solid interfaces, including cellulose and other polymeric surfaces. Special importance is attached to the existence of thermal anomalies in the vicinal properties of water.

On the other hand, Peters (85) has explored the effect of different heat treatments on the rate of dyeing of nylon 66 with different dye classes. Dry air and superheated steam have been found to decrease the dyeing rate, while heat setting in saturated steam has increased the rate of dyeing. In both cases crystallization increases and orientation decreases. By subjecting the samples to tension, the crystalline regions exhibit an increase in orientation while the

amorphous fractions become less oriented. Increasing the degree of order in a polymer decreases the rate of dyeing.

Disperse Dyes

This is a class of water insoluble dyes usually applied from a fine aqueous dispersion. They are generally ground in a mill to fine particle sizes ($1\ \mu - 10\ \mu$) in an aqueous medium containing a dispersing agent that stabilizes the dye suspension and acts as a restraining and retarding agent (1).

Disperse dyes are non-ionic components. They belong to three main classes, viz. nitroarylamine, azo and anthraquinone. Almost all disperse dyes contain amino- or substituted amino- groups, but they do not contain solubilizing groups such as sulfonic groups (1). In 1968, 50% of the disperse dyes used technologically were monoazo-, 25% were anthraquinone-, and 10% were disazo-compounds (93).

The principal uses of disperse dyes are the dyeing of cellulose acetate, nylon, polyester, and acrylic fibers (see Table 3 in Appendix A). Fastness properties to light and washing are generally good, although, disperse dyes have a very poor light fastness on cotton (31). The dyeing mechanism of hydrophobic fibers is believed to be one of solution in the fiber with no specific electrically charged dye sites being needed for dyeing to take place (1).

The required properties of disperse dyes are the following: high particle dispersion in dye bath without agglomeration to avoid specking, appropriate diffusivity, good levelling, and suitable sublimation fastness. Disperse dyes

containing hydrophobic groups have a relatively low melting point, high vapor pressure, and susceptibility towards sublimation (66, 90).

At the dyeing temperature, disperse dyes possess very low solubilities in aqueous dispersions. Dye associations have been found on applying pure disperse dyes on polyester; an increase in the particle size of the dyes was observed resulting in a lower aqueous solubility (28). This assumes that the rate of dyeing is directly related to the concentration of the dissolved dye molecules. Anomalies in rates of dyeing were inconsistent, and it is now suggested that the inconsistency may be explained by the formation of different structural modifications of the solid dye during dyeing (49).

Reactive Dyes

The major characteristic of a reactive dye is the electrophilic reactive group that causes the dye molecule to chemically combine with the nucleophilic functional group in the substrate. A bridge link attaches the reactive group to the chromophore that usually has water solubilizing groups to make the dye soluble in water (93).

The reactive groups in more than half the commercially available reactive dyes are chlorotriazinyl derivatives; nevertheless, a significant number of other reactive systems are now in use as reactive dyes (1).

The reactive system of the dye used in this work, Levafix Blue P-RA (C.I. Reactive Blue 104), is 2,4-difluoro-5-chloro-pyrimidine, called FCP for short. The FCP dyestuffs cover a wide range of reactivity (51). This can be done

by varying the bridge link which influences the reactivity of the reactive system. The dissociation of the imino bridge may reduce the reactivity of the reactive groups by several powers of ten. The influence of the chromophore on reactivity has also been reported (93).

After providing the dye molecule with the necessary affinity for the fiber it is supplied with the chromogenic (colored) portion. For the most part, the following are used: for yellow, orange, and red colors, simple, metal-free mono-azo dyes; for violet, ruby, and navy colors, cupriferous mono- and disazo dyes; and, for bright blue colors, anthraquinone derivatives. This may also apply to other classes of dyes (93). The disperse dye that has been used in this research work, Resolin Blue FBL (C.I. Disperse Blue 56, 63285), is a 1,5-diamino-4,8-dihydroxy-mono-chloro-anthraquinone.

Reactive dyes for cellulose and protein fibers have from one to four sulphonic groups to make them water soluble. This is necessary in order to transfer the dye molecule into the fiber in aqueous media (93).

Under the conditions of application, reactive dyes enter into chemical combination with the substrate, forming covalent bonds. In the case of cellulose, the reaction of the dye can be brought about by the addition of sodium bicarbonate to the dye bath and, with less reactive dyes, requiring higher dyeing temperatures, sodium carbonate is more frequently used. Dye remaining unattached by a covalency to the fiber is hydrolysed and must be thoroughly washed off the fiber; otherwise, poor fastness to rubbing and to wet treatments generally result (1).

Reactive dyes are usually used to dye cotton, rayon, wool, and silk fibers (see Table 3 in Appendix A). However, some reactive dyes may dye polyamides like nylon fibers (93).

Advantages of the reactive dyes are the following: almost an unlimited possibilities of shades, versatility of application either by batch or continuous processes, good levelness and penetration, reliability in application with good all-round properties, and comparatively little soiling of machine parts (50). Reactive dye bathes are relatively unstable although a neutral dye bath may remain stable for several hours. Reactive dyes are superior to some--particularly yellow--vat dyes that induce accelerated oxidation with subsequent tendering of the cellulose on exposure to light (103). Investigations have been made on the specific surface values of reactive dyes leading to the suggestion that these dyes exist as multilayers in cellulose (48).

Dyeing Cotton with Reactive Dyes

Reactive dyes primary adsorption on cotton is normally aided by salt, e.g. sodium chloride. Cellulose in cotton can be regarded as a polyhydric alcohol undergoing most of the reactions of alcohols. Thereupon, addition of alkali promotes ionization of hydroxyl groups in cellulose so that covalent bonds can form between the dye and the fiber (100), that is, the ionized hydroxyl group of cellulose, which has a nucleophilic character, adds to the electrophilic center of the reactive group in the dye molecule.

The reaction of halogeno triazinyl or diazinyl reactive systems with

cellulose is accomplished by the nucleophilic bimolecular substitution mechanism. The first step is the base catalysed addition, at a pH of about 10, of the nucleophilic cellulosic functional group to the reactive group of the dye. This is followed by the elimination of the nucleofugal halogen ion, which is also a base catalysed reaction (93). Usually, the unfixed portion of the dye is considered to be hydrolysed.

During reactive dyeing of cellulose, fixation competes with hydrolysis. Once the dye is hydrolysed, it cannot react with the fiber. Therefore, to have a high dyeing efficiency the ratio of the fixed dye to that of the hydrolysed should be as high as possible.

Less reactive groups should give a higher fixation (16), but their reaction rate is low; and, increasing the dyeing temperature to increase the fixation rate, has a reverse effect on the relative amount of dye fixed, or fixation. That is the hydrolysed portion of the dye increases with low substantivity dyes at high temperatures. On the other hand, a highly reactive dye that is highly substantive does not penetrate uniformly into the substrate and it becomes more difficult to remove the unfixed dye because of the build up of high negative potential zones, corresponding to non-uniform dye fixation, which opposes the hydrolysed dye transfer from the cellulosic structure (86). A chromophoric group with greater substantivity may counterbalance the unfavorable influence of high temperature on fixation of low reactivity dyes, but even so the less reactive systems give poorer fixation at high temperatures than very reactive systems at

low temperatures (93).

The reactivity of dyes based on halogeno triazinyl or diazinyl reactive systems can be increased by increasing the number of halogen atoms in the reactive group. The electron withdrawing properties of the nitrogen atoms bring about the reactivity of the halogen atoms. Where only one halogen atom remains, reaction with cellulose does not readily occur and dyeings may have to be done in the boil under more alkaline conditions than cold dyeings with highly reactive dye systems having two or three halogen atoms.

Effect of the pH on the dyeing system is similar to that of temperature, that is, increasing the pH will increase the rate, but will decrease the fixation efficiency. Under slightly acid conditions hydrolysis is at a minimum, but the reaction rate becomes very low (101). Nevertheless, it has been reported that increasing the pH, or the temperature, causes an increase in the diffusion coefficient; consequently, improving the overall efficiency of the dyeing operation (86, 87).

The washing resistance of reactive dyes is little affected by the solubilizing groups in the dye, but it rather depends on the stability of the dye-fiber linkage and efficient removal of occluded or adsorbed hydrolysed dye (37). Rate of acid or alkali hydrolysis of the dye-fiber bond must be negligible for a reactive dye to be useful; this can be achieved by attaining high fixation yields. Washing fastness is given special consideration for fabrics subject to alkaline washing, or resin finishing under acidic operating conditions (93). Halogeno

tri- or diazinyl reactive systems when fixed in the fiber give ester bonds, which are generally more stable to alkaline than to acid conditions (37).

Reactive dyes are tinctorially strong, this makes the washing out of even small amounts of dye difficult, unless electrolytes and free alkali in the bath surrounding the dyed substrate are efficiently removed (37). Washing of the fiber is usually made by soaping at temperatures above 90 deg. C while using anionic and/or non-ionic detergent followed by good rinsing (51).

Thus the improvement of the yield of fixation of reactive dyes on cellulose enhances the safety, reproducibility, and fastness of the dyeing. Hydrolysis formation has several undesirable effects on fastness and quality control (51).

Association of the reactive dye molecules in solution does not depend on the nature of the reactive group (84). The association reduces the rate of diffusion and makes the reactive residues less prone to hydrolysis with the medium and less available for reaction with the fiber (64). High dye concentrations promote association in the dyebath. It is now generally accepted that addition of urea to a reactive dyebath reduces the degree of association of the molecules thereby increasing the number of groups available for reaction with the substrate and improving the yield of reacted dye (5).

Dyeing Polyester with Disperse Dyes

Polyester had offered considerable difficulties in dyeing. Due to the lack of hydrophilic properties, the fiber has a greater electro-negative surface charge in water; accordingly, it has no affinity for direct dyes (93). Furthermore,

it has no reactive groups such as those present in cellulose or protein fibers (76).

Disperse dyes applied from an aqueous dispersion are transferred from the suspended aggregate, in the molecular form, to the fiber, forming a solid solution in it. This is due to the greater affinity that the dye molecule has for the organic fiber than for water in the dyebath (76). Suggestions have been made that hydrogen bonding and van der Waals forces might be also involved (103). This technique has been used for most of the synthetic fibers, but it did not prove to be easily applicable to polyester. Disperse dyes are still far more promising than vat dyes, since the disperse type are smaller in molecular size and can build up to full shades (104).

The polymer chains in polyester are much more closely packed than most of the other polymeric fibers. Polyester fibers have a relatively high degree of crystallinity of about 60%, (7). The long chain molecules are neatly packed in a zig-zag pattern, having no gaps that will suitably accommodate the dyestuff molecule; moreover, the chain molecules are very reluctant to change their positions. The result is that the dyeing process becomes so slow that it takes a matter of days or even weeks to dye polyester with disperse dyes at a temperature of 85 deg. C (76).

Several dyeing processes have been developed to overcome the difficulties of dyeing polyester with disperse dyes, viz., use of high affinity dyes, pressure dyeing, carrier dyeing, and thermofixation.

Disperse dyes with high affinity for polyester can be applied to give

light to medium shades in about one and a half hours at the boil. A temperature of 100 deg. C is necessary for the dyeing to take place; otherwise, if a lower temperature is used, most of the dyestuff will be on the fiber surface, resulting in a very poor rubbing fastness (76).

In aqueous media at higher temperatures, say 120 deg. C, more energy is given to the chain molecules, providing enough space in the polymeric structure to accommodate the dye, which also acquires a higher diffusivity. The dyestuff can penetrate the fiber well so that good medium and heavy shades can be obtained within a reasonable dyeing time of, say, one hour. Such processes require pressure dyeing equipment, which are not so well developed for continuous dyeing (76).

The use of the carrier allows the chain molecules to move farther apart so that the diameter of the fiber increases; thereby, creating more space to contain the dyestuff molecule. Advantages of carrier dyeing are the following: shorter dyeing time, very good dye penetration, improved levelling, and no special dyeing equipment are necessary. On the other hand, carrier dyeing has some disadvantages; considerable extra cost, difficult removal of the carrier, undesirable effects on light fastness, and pollution (76).

Thermofixation methods of dyeing are most suitable for the continuous dyeing of polyester. The fabric is first padded with the disperse dye in the presence of a thickening agent to maintain a uniform dispersion on the fabric. After drying the fabric, it is passed through a chamber where dry air or superheated

steam is circulated at temperatures varying from 175 deg. C to 200 deg. C for a residence time of one minute, this is followed by soaping then washing (103). Fibers which are most difficult to dye generally give the fastest dyeings.

Scouring of polyester before dyeing, is necessary to remove traces of the different finishing agents used to facilitate the fiber processing, viz. anti-static agents, and other oily ingredients frequently used. Some disperse dyes dissolve in these ingredients resulting in poor rubbing fastness or a change in color (57).

Changes in the profile shape with time for a number of disperse dyes on polyester filaments have been made; horizontal profiles were obtained (12). The profile shape and the observation that in all cases the dye concentration at the surface is time dependent, showed that the rate of dye transport to a boundary just within the surface of the substrate is not higher than the rate of dye transfer to the interior of the fiber. This behavior leads to the assumption either that the substrate is behaving like a liquid, or that the driving force for diffusion is an activity gradient and not a concentration gradient of the diffusing species. By plotting the concentration of the adsorbed dye in polyester versus the concentration of the dye in the dyeing bath, linear isotherms are obtained up to the point of saturation (57, 26).

The heat-setting temperature of polyester largely affects its dye uptake; the uptake first decreases as the setting temperature is increased, but increases again at higher heat-setting temperatures until it equals or exceeds that of an

untreated control sample (72). It has been found that the thermal history of polyester to some extent controls not only the rate of dyeing, but also the related migration and levelling properties of the dye within the substrate (58). In addition, heat treatments affect the glass transition temperature (T_g), which is directly related to the molecular order of the polymer, i.e., orientation and crystallization. It is usually determined on the dry polymer. In heated environments either aqueous or gaseous, such as dyeing systems, T_g may be considerably lowered (58).

Dyeing Polyester-Cotton Blends

The criteria for choosing a dyeing process are as follows: kind of shade, degree of fastness, quality requirement and control, price level involved, and equipment availability. Selection of the dyes to be used greatly affects the process design (51).

Generally speaking, continuous dyeing of polyester-cotton blends is more economic and reduces the source of error, especially when large yardage, constant quality of goods, and the necessary equipment are available. However, goods are not matched off after dyeing and faulty dyeings are virtually irreparable. In some cases it is possible to provide better control by splitting up the entire process into individual phases. Semi-continuous processes might be safer, but they result in higher operating costs. A common unit process in all continuous dyeings is the thermofixation of the disperse dyestuff in the polyester component, the differences are in the dye fixation of the cellulosic portion

of the blend (51). Although, different dye combinations can be used.

Vat dyes are suitable for dark shades on cotton, but they stain polyester, that is, cotton can not be dyed with the polyester left white. Higher temperatures, as in thermofixation, result in heavy staining of polyester (3). In light shades, the vat dye staining of polyester is as strong as the shade on cotton and can have fastness properties equal or superior to that of vat dyes on cotton (115, 8, 3). In addition, it has been found, from experience, that it takes a stronger reduction bath to reduce the vat dyes than it does with straight cotton, due to the pickup of the chemicals on the blend (112).

When disperse and vat dyes are used simultaneously on the blend, as the depth of the shade increases dyeing of the cotton component is insufficient and coverage becomes increasingly poorer; the vat dye stains polyester and the disperse dyestuff stains cotton (55). Furthermore, caustic soda and reducing agents required to fix the vat dye on the cotton may strip a substantial portion of the disperse dye from polyester resulting in a poor balance between the two fibers, particularly in heavier shades (56).

Soluble vat dyes (leuco-vats) on the blend have some limitations: shade change on finishing, low light fastness, light shades, and for some shades they are more expensive than a combination of vat and disperse dyes (115).

For dark shades, disperse and sulphur dyes are more suitable, economic for most end uses, and give a satisfactory fastness, although a good color balance is unlikely, since sulphur dyes stain polyester appreciably (115).

Disperse and azoic dye combinations are more difficult to apply; a two step fixation is necessary and special facilities are required to have a good yield. Bright red shades and sometimes dark shades can be obtained (115).

The use of reactive dyes for dyeing the cellulosic component of the blend competes with the use of sulphur dyes, vat, leuco-vat, and direct dyes. Polyester has no affinity for reactive dyes, and, by choosing appropriate disperse dyes the stain on cotton becomes negligible. A wide range of bright and even dark shades can be easily obtained with good fastness properties (51, 115).

Disperse dyes might not be stable under alkaline conditions, which are necessary for the reactive dye fixation on cotton, thereby staining the cotton portion excessively. Dyes which resist alkaline pH must be used; the dye should be stable for a reasonable period of time, say three hours, under the padding conditions (62, 82). Disperse dyes should produce minimum staining of cotton to maintain high fastness standards (82). Some disperse dyes with poor sublimation fastness are quite suitable for the continuous dyeing of polyester-cotton blends (66).

Disperse and reactive dye combinations are the most attractive for the simultaneous dyeing of cotton and polyester by thermofixation. The padding mixture can contain disperse dyes, reactive dyes, sodium bicarbonate, and for heavier shades some urea to give improved dye solubility and fixation (51).

In many dyeings the cellulose component of the blend has the main color effect, this is a result of the cotton fiber tendency to migrate to the sur-

face of the yarn during the yarn manufacture (81). The influence of the blending ratio can be minimized by improving the color balance (tone on tone) matching of both the cellulose and polyester component (51).

When both the disperse and reactive dyes are padded simultaneously, it is called a "one bath" method. A "two bath" method involves the padding of the two types of dyes separately. Fixation of both dyes at the same time is referred to as "one pass" dyeing, while fixing first the disperse dye and then the reactive dye is a "two pass" dyeing process. The less common dyeing technique is the two bath, two pass dyeing, in which the disperse dye is first padded and fixed, then the reactive dye is topped over and fixed separately. A more common process is the one bath, two pass dyeing, in which both disperse and reactive dyes are padded in the absence of alkali and the disperse dye is first fixed, followed by a chemical pad and dye fixation (51).

The one bath, one pass method of dyeing polyester-cotton blends with disperse-reactive dye systems is very attractive for the low cost involved as well as the simplicity of the method. After padding the dyes and auxiliaries the material is dried and thermofixation occurs either in dry air (Thermosol or baking), or in superheated steam (HT-steaming), then washing and rinsing follows as usual. Although, the process restricts the dyer to a relatively limited number of dyes, nevertheless, the process is becoming increasingly popular in the dyeing industry. New dyes with suitable kinetic properties resulting in shorter reaction times for the continuous dyeing of the blend have been devel-

oped (51).

Preparation of the blend for dyeing is very important; the fibers are made absorbent by removing oil and dirt (104). This is usually done by scouring in the presence of alkali, e.g. sodium hydroxide or sodium carbonate, and other detergents. The concentration of the alkali used for scouring the blend is considerably lower than that used for straight cotton to avoid degradation of the polyester fiber. Polyester is susceptible to hydrolysis, which may result in a severe and rapid loss of the fiber strength (22). Scouring with solvent is an elegant but expensive preparation; solvent scouring of the blend with trichloroethylene cleans up polyester and removes oligomers--common impurities in polyester. In addition, it dissolves fats and waxes from the cotton component (111).

Well controlled mercerization causes little or no damage to the polyester; although the fibers become slightly yellowish (22). Advantages of mercerization are as follows: higher color yields are achieved on cotton due to increased dye substantivity, better fastness dyeings are produced, development of luster resulting from the swelling of the cotton fibers, and more dimensional stability is accomplished (36). On the other hand, some consideration should be given to the cost of chemicals involved, extra machinery required, increased operating costs, and effluent control (33).

Migration

In the process of dyeing polyester-cotton blends, two forms of dye migration occur, viz., particulate migration, during drying, and molecular migration, in thermofixation. The particulate migration should be minimized as much as possible; it can cause specking, nonuniform color distribution, changing in union between polyester and cotton (cross-dyeing), and very poor surface appearance (112). Particulate migration is more pronounced on fabrics than on yarns. Disperse dyes exhibit a stronger tendency to migrate, due to their relatively small size, than reactive dyes (52).

After the polyester-cotton blend has been impregnated with the dye dispersion, ideally, the dye particles are uniformly distributed throughout the fabric. If both sides of the fabric are subject to equal drying conditions, water evaporation will occur at the exterior fabric surfaces; thereby, forming water concentration gradients between the interior and exterior of the fabric, which will drive unbound water to the fabric surfaces. At the same time, dye particles are carried with the flowing water and deposited at the surfaces of evaporation (32).

In the case of yarns, due to coring, the yarn surface may consist of 20% polyester and 80% cotton, even though the total percentage composition of the yarn is 50%-50% polyester-cotton. During the drying of such a blend, water will be driven out of the polyester, which has very little affinity for water, to the cotton component, where it will evaporate to the surrounding; from

the exposed surfaces of cotton fibers. After drying, the interior of the yarn, mainly composed of polyester, will contain much less dye liquor than the exterior (23).

During thermofixation, individual dye molecules separate from the solid particulate dye phase and evaporate to the surrounding before adsorption on the polyester surface occurs; due to the high affinity of polyester for the disperse dye vapor. Molecular migration is generally in the vapor form, although dye diffusion through a solvent may occur when there is a liquid phase (32).

If during the drying step a significant movement of dye to the yarn surface has occurred, during thermofixation the deposited dye is redistributed in the yarn interior for good fixation to occur, especially for fabrics containing yarns in which polyester is cored (32). The dye molecule movement to the fiber interior (out-to-in movement) is relatively slow; it is controlled by the vapor pressure of the dye in the monomolecular form and the available surface for adsorption. The out-to-in dye movement is proportional to both the dye vapor pressure and the amount of dye available per unit surface of polyester fibers (9).

Dye migration is usually controlled by using special antimigrant additives, increasing the viscosity of the dye bath, adding salt to the bath, using selected disperse dyes, decreasing the wet pick-up, and performing uniform drying (91). Antimigration products are sometimes called thickeners; the products are actually thickeners but function as migration inhibitors (115). Nevertheless, some surface active agents are used as antimigrant additives. Increasing the dye

bath viscosity by adding thickeners such as alginates or vegetable gums contribute in reducing dye migration. The effect of these additives might be attributed to the decreased dye agglomeration (115). Addition of salts, e.g. sodium acetate or sodium chloride, reduces the stability of disperse dye suspensions and therefore is an undesirable method for controlling migration (88, 115).

Since the extent of particulate migration depends on the moisture content of the fibers, the wet pick-up should be lowered as much as possible, e.g. from 50% to 60% (88). Disperse dyes have a strong tendency to migrate as the residual moisture content goes above 35% (52).

Dyeing Auxiliaries

Thickeners

Conventionally, every pad bath will contain a suitable quantity of thickeners (62). Thickening agents are added to ensure adequate and uniform absorption of the dye dispersion by the polyester portion of the blend. The capacity of the thickener to retain the dye particles in the fibrous structure opposes the tendency of water to entrain the dye during drying; thereby, retarding the dye migration and producing smoother shades. As a rule, thickeners help obtaining more even dyeings, especially in the case of pale shades (105).

The most common thickening agents used are alginate, acrylate, and natural gum thickeners (62). Commercial thickeners are usually strongly alkaline and contain buffering compounds, which make a simple pH adjustment with acetic acid or formic acid difficult (73). Thickeners impairing the pad liquor

stability, the dyestuff yield, or the dye dispersion, should be avoided as much as possible. The choice of thickening agents seems limited (73, 105).

Urea

Studies have been made on the effect of additives such as urea (80), formamide (71), and alcohols (13) on the structure and properties of reactive dye solutions. Additives of this type have been found to induce disorientation of the water structure in the vicinity of the dye ion; thereby, reducing the dye aggregation by decreasing the compactness and increasing the mobility of the surrounding water molecules--a direct result of disorientation. Similarly, a disorientation of the water molecules surrounding the disperse dye in the dye bath decreases the hydrogen bonding of the water structure around non-ionic dye particles and results in dissolution of the disperse dye aggregate, due to the loss of hydrophobic interactions (37, 86). Although this mechanism has not been conclusively proved, there is no doubt that the presence of urea decreases the dye-dye interaction and leads to increased rates of dyeing (21).

Addition of urea to a reactive dye bath reduces the degree of association of the molecules, consequently, increasing the number of reactive groups available for reaction with cellulose and improving the yield of the reactive dye (5). It has been reported that the influence of urea in improving the efficiency of reactive dyeing cannot be due solely to an increase in the dye solubility, or dissociation, but it is attributed to an increase in the dye diffusion coefficient on increasing the dye concentration in the bath (63).

It has been found that in aqueous media and in the presence of urea, the relative diffusivity of disperse dyes in polyester decreases, despite the fact that urea causes an increase in the rate of dyeing (21). A suggestion has been made that urea accelerates dyeing by influencing parameters such as the structure of the boundary layer in the vicinity of the substrate as well as the sorbate; thereby, increasing the accessibility of the disperse dye from the external aqueous phase to the fiber surface, while having an opposing effect on the dye structure inside the polymer (21, 57).

The presence of urea enhances the tendency of highly reactive dyes to interact with amino- or hydroxyl groups at certain positions in the disperse dye molecule, *either in the pad liquor, or in subsequent drying and thermofixation.* Nevertheless, satisfactory compromises in urea content can be obtained for specific dyeings (37).

Carriers

A common effect of a carrier on a polyester fiber is swelling, but the effectiveness of a carrier is not directly correlated to swelling proper, however, there are special fiber swelling agents that are added to give shorter thermofixation times (43). The important actions of a carrier on a fiber are to facilitate the motion of the chain molecules in the polymeric structure by reducing the intermolecular bonding, to lower the polymer glass transition temperature, and to solubilize the disperse dye on the surface of the fiber. Apparently, no simple correlation exists between the effectiveness of a particular chemical substance

as a carrier and the effects just mentioned (27).

An ideal carrier is not expected to only increase the color yield, other requirements are as follows: low operating costs, easy removal from the fiber, no impairment of the fiber physical properties or dye fastness, nontoxicity, and biodegradability. No product has been found to meet all these requirements. The selection of a carrier is a compromise (27).

The incomplete removal of many carriers results in a reduction of the light fastness of disperse dyes on polyester (7, 66). In addition, irreversible changes in polyester structure have been observed in carrier dyeing with disperse dyes (15).

Surfactants

Surfactants are labeled according to their expected role in the finishing process, i.e., dyeing retarders, wetting agents, antimigration agents, detergents, emulsifiers, softening agents, bactericides, water-repellent finishes, etc. (76).

Anionic and nonionic surfactants are the most widely used. Cationic surfactants are costly and the less used; although they do not exhibit very good detergent properties, they improve the hand of fabrics during final rinsing and, in some cases, help in the dye fixation. Nonionic surfactants are not easily biodegradable and very prone to foaming, especially in the presence of anionic substances. Anionic surfactants are widely used, particularly the more recent type, linear alkyl benzene sulphonate (LAS), which is readily biodegraded

during sewage treatments and less susceptible to foaming (76).

In dyeing, surface active agents make the water phase more attractive for the dye molecule, thereby reducing the amount of dye adsorbed by the substrate at equilibrium (103). Anionic surface active agents improve the penetration characteristics of the padding liquor by facilitating the removal of occluded air from the fibrous structure of the material (39, 98), and increase the solubility of nonionic dyes, e.g. disperse dyes, but little is known about the state of the dye molecule under these conditions (58). In addition, anionic surfactants have very effective migration preventing properties, even in the presence of urea (98).

Addition of surfactants to the padding liquor for dyeing polyester-cotton blends causes difficulties, especially in the presence of thickeners, which stabilize any produced foam, using an antifoaming agent might result in undesirable staining on the blend (52).

Dispersing Agents

It is obvious that there are no distinct lines between thickeners, surfactants, and dispersing agents, since they could be classified as colloids, which form in the water medium hydrophobic or hydrophilic sols; characterized by light scattering properties (49).

The stability of dispersing agents depends on the charges available on the colloid particles. For hydrophilic sols, the solvating layers of water (hydration) help to prevent the individual particles from agglomeration. Whereas

for hydrophobic sols such solvation is unimportant, and only the electrical effect operates. This is due to the existence of differently charged layers at the solid-liquid boundary, which are formed by a charged, extremely thin layer almost fixed to the solid surface, and succeeded by a diffuse layer oppositely charged that extends some distance in the liquid phase, but the distribution of positive and negative charges is not uniform, since the electrostatic field at the solid surface will result in a preferential attraction of charges of opposite sign. Therefore, each colloid particle has a net charge on it; and because of the electrostatic repulsion between these charges, the particles cannot easily come together. Nevertheless, agglomeration, or flocculation, can be made to occur by adding an electrolyte, particularly one with highly charged ions having opposite signs to those of the colloid particles. These added charges will surround the colloid and decrease its double layer potential (zeta potential); causing the colloid particles to approach one another. Small quantities of electrolytes can strongly affect hydrophobic sols precipitation, while hydrophilic sols are slightly affected, however, large amounts of electrolytes may cause their agglomeration, which is exhibited by a sharp decrease in their viscosity. Furthermore, it has been found that alcohols and acetone, which are known to combine with water, cause a remarkable reduction in the viscosity of hydrophilic sols, due to the decrease in colloid hydration, and the addition of small amounts of electrolytes, under these conditions, results in agglomeration (49).

In an aqueous medium, dispersing agents form micelles that enclose

disperse dye particles; a great multitude of colloid molecules surround the non-ionic particles, so that the charged ends of the colloid are directed towards the bulk of the liquid phase, consequently, because of the electrostatic repulsion, micelles stay apart and do not agglomerate any further (49).

Furthermore, dispersing agents increase the disperse dye solubility, or hydration, thereby acting as dyeing retarders, especially during exhaust dyeings. On the other hand, dispersing agents should be carefully selected to minimize their interaction with other chemicals in the padding bath, particularly the reactive dyes during thermofixation of polyester-cotton blends (51).

Thermofixation

Mechanism

General. During padding, cellulose picks up more dye liquor than the polyester portion due to its imbibition properties (68). While drying, the padding liquor transfers from the polyester to cellulosic fibers (24). Whereas in thermofixation, most of the disperse dye fixed on polyester is transported in the vapor phase from the cellulosic component (11, 24, 25).

Bent et al. (11), showed how the disperse dye vapor is transported over large voids, or air gaps between fibers. The disperse dye molecules separate from the dye dispersion and leave the cellulosic surface to the vapor phase. Part of this vapor is loss to the atmosphere and the other part, due to the affinity of the dye vapor to polyester, is adsorbed by the polyester fiber surface and penetrates the polyester interior by diffusion. At the same time, a small amount

of the disperse dye vapor finds its way in the cellulose interior by diffusion. The dye transfer by fiber-fiber contact or via layers of molten additives is negligible and has been dispelled as a mechanism to explain the accelerated disperse dye transfer into polyester during thermofixation (37).

The heat of sublimation fastness is the most important factor affecting the efficiency of the disperse dye transfer during thermofixation. A dye with a too low vapor pressure, at the operating temperature, will be insufficiently transferred and will remain on the cellulosic portion. On the other hand, a dye with too high a vapor pressure will be lost to the atmosphere and may as well precipitate on the cooler parts of the equipment. A desirable disperse dye would be completely vaporized from cellulose and fixed into polyester under the operating conditions. The disperse dye that stays in the cellulosic portion after thermofixation is very difficult to remove during subsequent wet treatments, and this will affect the fastness properties of the dyed blend (68).

It is important to keep in mind that the physical phenomena of dye transport or molecular rearrangements are all accelerated by increasing the fiber temperature as well as moisture content (75).

Hot Air Thermofixation. Datye (23) and Bent et al. (11), have investigated the dyeing mechanism of polyester during hot air thermofixation. A linear relation between the amount of dye absorbed by polyester and the distance from the dye source was observed. By extrapolating to zero distance, the amount of dye absorbed by polyester was found to agree with the experimental result when

the polyester and dye are in contact. Bent et al. results lead to the conclusion that the amount of dye absorbed can be explained by a single transfer mechanism via vaporization and absorption of dye vapor by polyester. Datye's results showed an additional small contribution by a direct contact mechanism. Furthermore, it has been found that the dispersing agents or different migration inhibitors have no effect on the rate of dye vapor transfer to the polyester (23).

Superheated Steam Thermofixation. The contact of a cold fiber with superheated steam at atmospheric pressure, causes immediate steam condensation on the fiber to occur, resulting in virtually instantaneous heating of the fiber to 100 deg. C. Then vaporization of the condensed water begins; during this time the fiber temperature remains unchanged. Only after the condensate evaporates, does the fiber start heating up to the ambient temperature (7, 69, 75).

When the padded blend enters the HT-steamer condensation occurs; the volume of condensed water depends on the original fiber temperature and moisture content, the specific heat of the padded blend, structure of the fabric and yarn, and the dyestuffs and auxiliaries applied (75, 7).

On condensing, water releases its latent heat to the fibers, 539 cal/g, which causes the spontaneous raising of the blend temperature to 100 deg. C; although, if the steam is air free and at atmospheric pressure, the temperature may rise to higher values if exothermic reactions follow. The absorption of water by cotton is exothermic and the heat evolved might very well raise the temperature to a higher value, e.g. 120 deg. C (75). Furthermore, salts and organic com-

ponents that dissolve in the condensed water, will generate heat of solution. It has been found that in the presence of glycerol and salts like potassium carbonate, which elevate the boiling point of water, temperatures as high as 130 deg. C can be reached (74). Prediction of the temperature variation with time for such a complex system is difficult and equilibrium is unlikely to occur, especially during the early stages of the process (75).

The more superheated the steam is, the less water will condense on the blend. The first condensate droplets forming on the fibers will raise the temperature to the boiling point of water by virtue of essentially the latent heat, but the temperature gradient between the condensate, at about 100 deg. C, and the surrounding steam, say at 200 deg. C, will cause a considerable amount of sensible heat to flow; thereby, accelerating the condensate evaporation, by comparison to saturated steam, and raising the fibers temperature to 200 deg. C (75).

From the observations made during superheated steam thermofixation, several explanations have been suggested to elucidate the dyeing mechanism under different conditions.

In the presence of urea, the condensed water and urea form an eutectic mixture in which disperse and reactive dyes dissolve to different extents. It has been suggested that this melt increases significantly the rate at which the dyes diffuse into the fiber substrate (69). Disperse dyes have been shown to be essentially transported to polyester in a vapor phase rather than molten urea (11, 23).

During the evaporation of the condensed water, the temperature remains unchanged and a certain swelling of the thickening agent takes place; providing favorable conditions for diffusion of the dye particles into the fiber (7).

The water absorbed from the condensed steam has three separate functions on both the fiber and padded liquor. Inter molecular polar bonds between the polymer chain molecules, especially hydrogen bonds, are broken, and water molecules are infiltrated into the structure bringing about fiber swelling and increasing the polymer chain mobility. Dry films of padded dyestuffs and auxiliaries are swollen and dissolved with water. The water acts as a transport and reaction medium for the dye-fiber interactions to take place (75).

Vapor Pressure Effect. The heat transfer rates of hot air and superheated steam are very similar (4); therefore, it is unlikely that a slight difference between the two heating media produces the observed increase in dye fixation rates that occurs in superheated steam. Nevertheless, mixing steam with even small amounts of air, causes a sharp decrease in the dye fixation (69). On the other hand, the presence of water vapor during hot air thermofixation, reduces the amount of disperse dye adsorbed by polyester because of the possible competition between sorbate and water and changes in substrate structure enhanced by the presence of water (59).

Rapid attainment of high dye saturation values during HT-steaming can be accomplished by maintaining the steam content as near to 100% as possible (69). Similarly, high fixation yields are obtained in baking by minimizing

the water vapor content as much as possible (59).

It has been found that the total amount of disperse dye adsorbed by polyester from a mixture of disperse dyes during hot air thermofixation is less and requires longer fixation times than when a dye is applied separately. These observations lead to the suggestion that the perceived reduction of the dye vapor pressure, due to the presence of other dye components in the vapor phase, might induce a solid-solid transition to that of a more stable polymorph (61).

Intermediate Drying. Uniform drying of polyester-cotton blends is very difficult to perform with hot air circulation, and particulate migration is promoted, whereas infrared drying has proven to be more successful in controlling the dye migration (88). Nonetheless, drying after padding leads to undesirable dye migration, especially in pale shades, unless a thickener with a small amount of wetting agent is added to the padding liquor (56). Excessive migration on a blended fabric is exhibited by the presence of halos around the slubs, cross shading, and back-to-face shading, which is an indication of insufficient thickener in the pad bath, or inappropriate drying (42, 55).

To minimize migration during drying of the blend, the water evaporation should be as fast as possible, consistent with uniformity. Furthermore, the residual moisture content should not exceed 35%, otherwise, there remains an inherent tendency for the dye migration to dryer portions. There is no migration to worry about once the moisture content has been reduced to 30% (105). However, if the moisture content is much below 30% in the infrared zone of

the dryer, hardening of the thickener can occur, which is not advantageous at such an early stage, particularly before HT-steaming (68).

A disadvantage of intermediate drying before superheated steam thermofixation is that, owing to the very small quantity of water condensing on the blend as it enters the HT-steamer, the reactive dye penetrates the cellulosic fiber much more slowly than it does in the case of wet fibers (43). Significantly better fixation yields have been obtained by padding cotton with the reactive dye and fixing the latter with no intermediate drying (82). Allowing the blend to enter the HT-steamer with a moisture content of about 4% to 7% increases the disperse dye fixation yield (68). In general, the intermediate drying before steaming would result in longer fixation times than without drying (43). Nevertheless, there is no advantage in using the HT-steamer for drying and fixing disperse dyes on the polyester portion of the blend, since the dye fixation and diffusion do not occur under the drying conditions. However, this process might be advantageous for the fixation of reactive dyes on the cellulosic component (43, 82).

pH Effect. The one bath, two pass dyeing method gives better fixation of reactive dyes on the cellulosic portion than the one bath, one pass method, due to side reactions between the reactive dye, disperse dye, and dispersing agents under alkaline conditions during thermofixation. In addition, some disperse dyes are not stable under alkaline pH at high temperatures (51, 104).

Quantitatively, the side reaction products resulting from the interaction

between the reactive and disperse dye is relatively small, and the colored compounds formed are easily washed off. The corresponding yield loss is negligible when compared to the advantages of using the one bath, one pass dyeing process (51).

The pH level plays an important role in continuous dyeing techniques of the blend. In the one bath, two pass dyeing, a neutral or slightly acidic pH must be maintained in case of commercial dyestuffs to prevent premature reactions of the reactive dye during thermofixation (51, 62). Using phosphate salts for weakly acid adjustments results in a reaction between the buffer and cellulose at high temperatures such as 200 deg. C. This impairs the reactive dye yield on cellulose due to the induced phosphate modification of the cellulosic fiber. Acetic acid has been suggested as more suitable under thermofixation conditions (51).

In the one bath, one pass dyeing process of the blend, the alkali content of the padding liquor should be as low as possible to avoid the disperse dye degradation, and as high as necessary, to fix the reactive dye on cellulose. The pH value of 10.2 should not be exceeded under the thermofixation conditions, otherwise serious damage of polyester and decrease of the dyes yield will occur. Borax produces pH values between 8.9 pH to 9.3 pH which is too low for most reactive dyes, whereas trisodium phosphate and sodium carbonate give too high a pH. Sodium bicarbonate has been particularly successful as an alkali source, it can produce a relatively low 8.2 pH in the pad bath, which increases to 9.3 pH on the blend during thermofixation, without exceeding the 10.2 pH level; thereby,

no more than 10 g/l. should be used in the bath. Less alkali should be used for lower reactive dye concentrations (51).

Auxiliaries. With well prepared polyester-cotton blends the only auxiliary normally needed is a migration controller. Thickeners should not be used in excessive amounts in order to avoid undesirable dye aggregation and the poor appearance that the thickener was intended to prevent (68).

Thickening agents become very hard after thermofixation and are usually sparingly soluble in water. They are removed from the goods with the aid of a suitable emulsifier and dispersing agent in hot water at about 90 deg. C, this may be assisted by vigorous mechanical action (102).

Organic polyelectrolytes, e.g. sodium alginate, are recommended as migration inhibitors, since they prevent the dye particles aggregation. During thermofixation, the thickener forms a continuous film on the fibers that does not melt at the fixation temperature. The film surrounds the dye particles, and as long as it is not too thick, it does not interfere with the vaporization of disperse dyes from cellulose to polyester. The film formed redissolves readily in a neutral or alkaline rinsing (107).

Sodium alginate is a widely used thickener, especially in printing, since it results in satisfactory thermofixation yields with a wide range of disperse and reactive dyes, good brightness, no effect on hand or fastness properties, and easy removal in conventional washing processes (2).

In some cases, water alone may not be capable of bringing about the

dye yield requirement, and other agents, e.g. carriers and solvents, are added to increase the polymer chain mobility. Humectants, e.g. glycerol, are sometimes also added to achieve satisfactory dye yields in HT-steaming (75).

The action of a carrier during thermofixation is to loosen the internal structure of the hydrophobic fiber. After being absorbed, the carrier replaces the interchain bonds with more readily disrupted chain-carrier bonds. With increasing mobility, due to thermal agitation, the number of openings will increase under the same thermal energy; resulting in a more permeable fiber and greater dye diffusion (79).

Certain anionic surfactants help in dissociating the disperse dye to the monomolecular form and in transferring it from the fiber surface to the fiber interior; thus, lowering significantly the energy requirement during thermofixation (109). Such surfactants ensure good dye penetration and reduce the fixation temperature. Surface active agents usually cause foaming of the pad bath. However, anti-foaming agents should be chosen carefully so that they do not oppose the accelerating efficiency of surfactants (88).

Preparation. Proper preparation is an important requirement prior to any continuous dyeing. To obtain optimum fixation the material has to be scoured properly and if possible mercerized (17, 51). For light shades bleaching is necessary, whereas for medium and specially dark shades, mercerization is recommended to improve the general appearance and increase the dye yield (105).

Urea

Properties. Hydrotropic substances, e.g. urea and thiodiglycol (75), combine with water during HT-steaming and form an eutectic mixture at high temperatures, this increases the dye solubility and inhibits association of the dye molecules (2, 69); thereby, giving a medium that accelerates the dye transfer from the layer of dry thickener to the fiber interior and results in better penetration along with uniform dyeings. This was exhibited by a decrease in the visual color yield of the material and an increase in the dye yield (82).

Advantages. By comparison with other auxiliaries that increase the thermofixation yield, advantages of urea are as follows: cheapness and availability, immediate dissolution in the padding liquor, the need for carrier addition is reduced or eliminated, easy removal from goods, and no adverse effect on light fastness. Furthermore, urea has been found to increase the rate of heat transfer to the material by reducing the time necessary to evaporate the condensed water in the HT-steamer. However, the temperature reached by the material after drying becomes slightly lower, this has been suggested to be a result of the slow decomposition and evaporation of the molten urea at the high temperatures usually employed in HT-steaming (69).

Effect on Disperse and Reactive Dyes. Urea should be as much as required and as little as possible. The addition of urea to the padding liquor improves the fixation yield of reactive dyes and reduces the time and temperature needed for their fixation (51, 98). Urea is indispensable to obtain high fixation

yields with low substantivity reactive dyes on cellulose during hot air thermofixation (51). Nevertheless, Kissa (63) has shown how urea can decrease the thermofixation yield of some reactive dyes forming ether type linkages with cellulose, e.g. dyes containing vinyl reactive groups, whereas, dyes that form ester bonds, e.g. amide halide types of reactive groups as in dyes bearing halogeno di- or triazinyl groups, are only slightly affected.

At lower thermofixation temperatures, e.g. 150 deg. C, the presence of urea in the pad bath improves disperse dye fixation yields, but at higher temperatures, e.g. 200 deg. C, the addition of urea decreases the disperse dye yield on polyester (82). However, urea increases the reactive dye fixation on the cellulosic portion at higher temperatures (51, 82).

Cotton Staining. Small amounts of urea have been found to decrease staining of the cotton portion in the blend by disperse dyes (105). Larger amounts of urea, especially in the presence of alkali, promote the cellulose staining (102). Urea has a greater effect on staining than alkali (98).

Carbamate Formation. At high thermofixation temperatures, e.g. 200 deg. C, the cellulosic portion of the blend reacts with urea, which results in the formation of cellulose carbamate that catalyses the reactive dye destruction by hypochlorite bleaching. The rate of carbamate formation at lower temperatures, e.g. 120 deg. C, is negligible when compared to the reactive dye fixation rate, but low temperatures will require longer fixation times, e.g. 6 min, and only disperse dyes with very low heat fastness could be used to fix on the

polyester portion of the blend (39, 40, 82).

Fibers Discoloration. The presence of urea reduces the risk of discoloration (usually browning) of the cotton component caused by alkali at high thermofixation temperature (98). Omission or reduction of urea increases the blend discoloration, so that the production of bright pale shades is rendered more difficult (82).

Effect on Drying and Thickeners. It has been noticed that the addition of urea, at relatively high concentrations above 50 g/l., decreases the drying rate of the material, and once dried, additional moisture absorption in the HT-steamer becomes difficult (2, 82). In addition, during drying and thermofixation, the thickening agent hardening is accelerated in the presence of urea (2), and at higher urea concentrations thickeners might be fixed on the fibers during thermofixation (75).

Equipment Contamination and Pollution. Large quantities of urea result in contamination of both the drying and thermofixation units (2, 75). Urea crystallizes on stationary parts of the equipment, necessitating regular deposit removal to prevent its accumulation. Deposits of urea are normally non-corrosive and can be easily washed off (2). In closed thermofixation units, the heating media are cleared from additives of higher specific gravity, e.g. urea, to avoid their precipitation on the goods, which could cause considerable damage to the dyed material (7). On the other hand, urea fumes evolved during thermofixation with open units may cause some nuisance (2).

Alternatives. Omitting urea is advantageous, but the range of dyes applicable becomes more limited (51). Another alternative might be the use of auxiliary dye solvents (surface active agents), however, the latter are not trouble-free and are more expensive (75).

Disperse Dyes

Properties Affecting Fixation. Factors influencing the disperse dye molecules fixation in polyester are as follows: molecular dimensions, volatility, and solubility in polyester (104).

The size and shape of the dye molecule will determine its capability to diffuse rapidly into the neatly packed zig-zag pattern of the polyester long chain molecules, under thermofixation conditions (104). Small dye molecules are generally easier to fix than large molecules (102). High thermal agitation opens up the polymer structure, which allows the disperse dye to penetrate more easily into the fiber (104).

During thermofixation the dye vaporizes from the cellulosic component to the polyester portion (98, 104). The dye vaporization depends on the dye molecule dimensions, dye concentration, time and temperature of thermofixation, and substrate. Disperse dyes of small size molecules are highly susceptible to sublimation. High dye concentrations, longer residence times, and elevated thermofixation temperatures enhance the dye vaporization. Disperse dyes on polyester exhibit a higher resistance to vaporization than similar dye concentrations on cotton. The dye on cotton has a low resistance to vaporization, but

the vaporized dye shows a greater affinity for polyester than cotton (98).

Disperse dyes of low sublimation temperatures are readily fixed to polyester at lower thermofixation temperatures for a given time, however, some of these dyes lose depth at higher temperatures due to sublimation (31). In addition, the dyes that fix at the lowest temperatures and shorter times, due to their very poor sublimation properties, result in cross shading effects (112). Dyes with the best sublimation fastness require higher fixation temperatures and result in good fastness properties (31).

The sublimation properties of a disperse dye are very difficult to measure and quantify. They are dependent on concentration, time and temperature relationships, whether heat is applied by conduction or convection, type of heating media used etc. (90).

Fixation Mechanism. Diffusion of disperse dyes into polyester fibers during thermofixation at 210 deg. C, has been found to be Fickian with a concentration independent diffusion coefficient. This is possibly the result of an increasing volume of voids arising from a high polymer segment mobility in the fiber structure (29).

A mechanism for the disperse dye transfer to polyester in HT-steaming has been proposed. It is known that most disperse dyes have a certain solubility in water at 130 deg. C during pressure dyeing. Similarly, the small amount of water that condenses on the blend as it enters the steamer (approximately 1% at 200 deg. C), may significantly affect the crystal form of the dye and conse-

quently its transfer to polyester (82).

Giles et al. (45, 46, 47) investigated the possibility of disperse dyes association in dyed polyester, by making measurements on the rate of fading (45, 46) and using other spectrophotometric techniques. The dye molecules first occupy the least ordered regions of the substrate and regions of higher orientation are only occupied at higher dye concentrations. On the other hand, Husy et al. results (54) indicated that the interaction between the dye and substrate molecules is more favored by a molecular dispersion than by a state of association.

Alkali Effect. Disperse dyes sensitive to alkaline conditions must be avoided, e.g. some azo disperse dyes are very susceptible to reduction in the presence of alkali during thermofixation (2). Many disperse dyes exhibit a decrease in yield and shade changes if the fixation is carried out in an alkaline or strongly acidic conditions, maximum fixation yield is attained under weakly acidic or neutral conditions (88). Nevertheless, the impairment of some commercial disperse dyes by alkali is unimportant, e.g. Resolin dyes, and several of these dyestuffs have pH values that are greater than 10 pH (51).

Reactive Dyes Interaction. Some disperse dyes of active hydroxyl or amino groups may react with halogeno triazinyl or diazinyl reactive dyestuffs, this should be taken into account when making the dyeing recipes (51). The usual result of interaction is loss of the color yield of both reactive and disperse dyes (51, 98).

Dispersing Agents. It has been found that the loss in the reactive dye fixation yield in one bath, one pass dyeing methods is mainly due to the dispersing agents incorporated with commercial disperse dyestuffs, since the drop in the reactive dye yield was proportional to the dispersing agent concentration. The concentration of dispersing agents in powder dye brands is three times that of dyes in the paste form. Liquid brands of disperse dyes contain the lowest concentration of dispersing agents. Therefore, under appropriate conditions they give better color yields than either powder or paste brands. On the other hand, powder and paste brand of disperse dyes are more versatile and convenient to handle than liquid dye brands (51, 88). By changing from powder to paste form of disperse dyes, an average increase in the reactive dye yield of 33% was observed (51).

The influence of the dispersing agents depends on the reactivity of the reactive dye and increases at higher thermofixation temperatures. The presence of amino- or phenol groups in the dispersing agent leads to substitution reactions with many reactive dyes (51).

In cases where the commercial disperse dye is responsible for insufficient fixation, two bath, two pass dyeing processes can be used, especially with highly reactive dyes. Nonetheless, compatible disperse and reactive dyes have been developed to produce satisfactory fixation yields with one bath, one pass dyeing methods; it has been found that some dispersing agents have a negligible effect on the reactive dye fixation (51).

Dispersing agents in commercial dyestuffs are high molecular weight

compounds containing ionized or polar groups at alternating positions with non-polar groups along the polymeric chain. During thermofixation the dispersing agent is adsorbed on the fiber, so that the molecular chains are oriented in parallel to the substrate surface, with the nonpolar groups adjoining the surface and the polar or ionized groups directed outwards. At high concentrations these compounds could act as barriers to the dye diffusion and reduce the overall dye fixation yield. The dispersing agents are necessary to prevent the disperse dye from precipitation, and their concentration must be maintained above a minimum in the padding liquor (107).

A significant brightening and often a change of shade occur upon washing off the blend after thermofixation. This takes place even in the absence of thickeners or other auxiliaries and may be due to additives incorporated with commercial dyes. Dispersing agents might be responsible, since liquid brands of disperse dyes give better results and less change in shade occurs after washing the blend (88).

Electrolyte Addition. Addition of electrolytes to the pad bath, to aid the reactive dye fixation, might cause some of the unfixed disperse dye to aggregate; resulting in low rubbing fastness properties, or dye spots on the blend, particularly in dark shades (68).

Cotton Staining. Disperse dyes staining of cotton is largely reduced by the different wet treatments following thermofixation. However, some of the disperse dye is mechanically embedded in the cellulosic fiber and is extremely

difficult to dislodge, even by repeated washing (102).

During the molecular migration of disperse dyes from cotton to polyester in thermofixation, disperse dyes of low melting point will actually penetrate the cotton fiber. The resulting staining reduces the light fastness and dulls the overall shade of the material (66). Increased staining of cotton may further reduce the wet and rubbing fastness (68). The drop in the fastness properties increases when reactive and disperse dyes are fixed simultaneously on the blend, especially with highly reactive dyes that are susceptible to reduction, e.g. by azo disperse dyes (66, 68).

Staining of cotton decreases at higher fixation temperatures and in the absence of carriers, which interfere with the disperse dye transfer from the cellulosic component to polyester (68). The use of disperse dyes in the paste form reduces the cotton staining due to the decrease in the dispersing agents concentration (66).

Reactive Dyes

Fixation with Disperse Dyes. In the one bath, one pass dyeing processes, most reactive dyes are fixed on cellulose, with the corresponding alkali consumption, during the early stages of thermofixation before the disperse dye start vaporizing and diffusing into polyester. This minimizes the interactions of reactive dyes and alkali with disperse dyestuffs, since aggregated disperse dye molecules surrounded by dispersing agents are less susceptible to interactions (51). Reactive dyes color the cellulosic portion only and leave polyester prac-

tically unaffected (102).

Moisture Content Effect. Generally, reactive dyes possessing high substantivity are large dye molecules; therefore, their rate of diffusion is highly improved in the presence of moisture on the fibers. Whereas dyes of low substantivity diffuse rapidly into the inside of the fiber during hot air thermofixation and give good yields, however, if saturated steam is used as a fixation medium they might bleed and hydrolyse during the transitory steam condensation on the fibers (51).

Fixation of highly reactive dyes on cotton in superheated steam reduces the opportunity of dye hydrolysis on the fiber surface, because the volume of the condensed water is small and the condensate vaporizes after a short time; thereby, conditions are more favorable for the dye fixation to take place and deep shades can be obtained. With low reactivity dyes, excellent diffusion of the dye into the fiber is prevailing during the stage of condensate evaporation at about 100 deg. C (82).

The stability of the reactive dye-fiber bond may be affected during HT-steaming and bond splitting, or hydrolysis could occur (51); therefore, reactive dye systems forming ether bond with cellulose are not recommended, since their resistance to alkali conditions is relatively low, but dyes that react with cellulose to form ester bonds are more advantageous, they exhibit a good resistance to hydrolysis and give better fixation yields (37).

Urea Effect. A significant improvement in the reactive color yield

has been observed by using HT-steaming, by comparison to other continuous thermofixation methods, even in the presence of relatively small amounts of urea. The reactive dyes have been found highly soluble in a melt formed by urea with small quantities of water, which improves the dye diffusion, and this is undoubtedly the reason for the increased rate of fixation in HT-steamers (82).

Interaction Products. The unfixed portion of the reactive dye, which is washed out of the blend after thermofixation, actually contains--beside the hydrolysed dye--several other products of interactions between the reactive dye and other chemicals present; disperse dye, dispersing agents, different auxiliaries, and impurities in the good. Most of these interactions are enhanced by the prevailing high thermofixation temperature. Thus, careful selection of different chemicals is essential and auxiliaries should not be added to the pad liquor formula unless it is necessary (51).

Bath Preparation. Preparation of the pad liquor for one bath, one pass dyeing method is important in order to prevent premature reactions from taking place. Best dissolution of the reactive dye is obtained with hot water. After cooling, the alkali, e.g. sodium bicarbonate, is added, and the resulting solution is then well mixed with a diluted disperse dye solution, eventually more water is added to bring the solution to its final volume (51).

Polyester

Heat-Setting. Polymeric fibers are formed of crystalline and amorphous regions. The macromolecules are arranged (oriented to different extents)

longitudinally along the fiber axis, and are crosslinked in the amorphous zones by hydrogen bonds. During processing, the fiber is mechanically deformed due to stretching, bending, or twisting; as a result, the distance between some of the linkage points is increased, creating internal stresses that will drive the fiber to regain its original shape once the deformation force is removed. When processed fibers are subjected to heat, as in thermofixation, lateral bond breakage of stressed linkages occurs promoted by high thermal agitation and, in the presence of steam, deposited water molecules causing fiber swelling. After the fiber has cooled off, lateral bond formation takes place at new sites corresponding to the required final shape (60).

The heat-setting efficiency of polyester increases with temperature and moisture content. An optimum setting temperature for polyester in dry air has been found to be at about 180 deg. C with a setting time from 30 sec to 40 sec (99). However, it has been reported that the molecular mobility of polyester at 150 deg. C in superheated steam under atmospheric pressure is more than that at 210 deg. C in dry air, suggesting better diffusional and heat-setting properties in a steam surrounding (75).

Pre-setting of the blend decreases the polyester component affinity for disperse dyes and results in levelling difficulties, in addition, longer exposure of polyester to superheated steam increases the risk of its hydrolysis (41). Nevertheless, the effect of pre-setting on the fiber affinity depends on the dye and dyeing procedure used. Thermofixation processes for dyeing makes it possible to

carry on dye fixation and heat-setting at the same time; thereby, reducing the possibility of fiber degradation, resulting in good levelling and higher dye yields (35). Furthermore, continuous dyeing with pressurized steam is usually followed by thermofixation to produce levelled dyeings, especially in heavy shades (106).

Melting Point. There is some indication that the presence of steam may lower the melting point of polyester, at least at the surface, which would enhance the disperse dye diffusion into the structure (82).

Padding the Blend. In padding polyester-cotton blends, less force should be applied on the pad rolls than during cotton padding, because of the low absorbancy properties of polyester (113).

Cotton

Preheating Treatments Effect on Fixation. By comparison to polyester, cotton fibers do not have press retention properties, particularly under wet conditions, heat-setting is intended to set the polyester fibers of the blend. However, cotton fibers may acquire press retention properties after dyeing by special resin finishes (53). Nonetheless, the cotton reactivity is affected by these heat treatments. After preheating the blend under different conditions, the reactive dye yield on the cotton component has been investigated; using the one bath, one pass dyeing method (51).

Drying moist goods, with 80% moisture content, using hot air resulted in no loss in the reactive dye fixation with respect to an untreated control sample,

whereas using contact heat resulted in a decrease of the fixation yield. Goods with higher moisture content exhibited a decrease in the dye fixation, whether using hot air or contact heat, particularly if drying is performed at high temperatures (51).

Heat-setting dry goods, with hot air at 200 deg. C, did not affect the fixation yield. Steaming dry goods decreased the dye yield, although, steaming moist goods increased the reactive dye fixation yield (51).

It has been suggested that at certain temperatures and moisture content values, prevailing under various heat treatment conditions, cellulose exhibits some modifications that are reflected by the reactive dye fixation yield (51).

To ensure uniform dyeing it is necessary to operate under steady conditions; the moisture content of the blend entering the drying unit should not change with time and the drying temperature should be well controlled. In addition, the drying must be uniform all over the full width of the goods, and high drying temperatures should be avoided (51).

The yield of highly reactive dyes has been found to be less influenced by different cotton heat treatments prior to thermofixation (51).

HT-Steaming. Steam condenses on the cold polyester-cotton blend, releasing its latent heat of condensation to the fibers, consequently, the temperature of the material rises rapidly to 100 deg. C. At the same time, if the blend has been dried prior to fixation, cotton will absorb some of the condensed water; evolving heat of absorption, since the wetting of cellulose is exothermic.

The cellulosic portion absorbs water in an attempt to reach the moisture content that satisfies the equilibrium conditions at 100 deg. C and 100% relative humidity, values of 18.5% to 23% moisture content have been quoted in literature. This additional heat of absorption raises the temperature of the material above 100 deg. C, thereby accelerating the condensate evaporation and dropping the cotton moisture content, which is inversely proportional to the ambient temperature. However, the rate at which the heat of absorption is evolved is less than the rate of water absorption by cotton. Therefore, more steam will condense on the material than expected on the assumption of simultaneous condensation and absorption, but not as much as would condense on an inert surface heated only by the latent heat. If the cotton fiber moisture content is below the equilibrium value, more condensate will be absorbed; thus, the material is heated by both the heat of wetting and the latent heat of condensation, raising the temperature as high as 110 deg. C or 120 deg. C (34, 75).

As the temperature rises, the value of the moisture content at equilibrium decreases, and the water content of cellulosic fibers starts falling quite slowly. The necessary heat of vaporization is supplied from the surrounding steam that is usually flowing at high volumetric rates to increase the rate of sensible heat transfer and accelerate vaporization. A net flow of sensible heat is transferred to the blend until it reaches the ambient temperature (75).

At high enough temperatures, hydrogen bonds between the chain molecules start breaking, the T_g of the polyester component is reduced, and the

structure becomes more accessible to the dye transfer (75).

Printers have known for many years that the steaming, at atmospheric pressure, of dry cotton (bach-greys) removes water droplets from the unsaturated steam and raises its temperature above 100 deg. C (75).

Advantages of HT-Steam

General. Water and steam thermodynamic properties favor their efficient heat energy and mass transfer between different phases, in multicomponent heterogeneous systems, under a wide range of conditions. They have been used preferentially over many other transfer media in the wet textile industry (95).

Disperse and Reactive Dyes Fixation. It has been shown that in both dyeing and printing, the superheated steam thermofixation gives higher disperse dye fixation yields on polyester than hot air thermofixation under the same conditions of temperature and residence time (2, 82, 97).

Compared with hot air thermofixation, the rate of disperse dyes fixation in polyester fibers by HT-steaming has been found to be higher; at equal residence times higher fixation temperatures were necessary for baking to yield similar dye fixation as in HT-steaming, similar results were obtained when fixing reactive dyes on cellulosic fibers (68, 77, 82). Nonetheless, if excessive temperatures and times are used, losses of the disperse dye vapor occur (38). On the other hand, the loss of disperse dyes by sublimation increases with increasing the air content in the superheated steam (69).

In addition, HT-steaming produces more brilliant shades, improves the

molecular migration of disperse dyes from cotton to polyester, results in more levelling and coverage of the dyed material (6, 68), causes less shrinkage and better hand (88), and helps in maintaining the reactive dye hypochlorite fastness when urea is needed, since fixation can be performed at lower temperatures and shorter times (82). Under the same dyeing conditions HT-steaming yields better fixation than baking, however, no difference in fastness properties has been observed (82).

Urea and Carriers. In HT-steaming less or no urea is necessary for the fixation of disperse-reactive dye systems on polyester-cotton blends; thereby, resulting in a better working atmosphere (37). In baking, more urea is needed for reactive dyes fixation in the cotton portion, whereas HT-steaming results in better dye fixation with or without urea (82). Similarly, compared to baking, less or no carrier is required in HT-steaming for fixation of disperse dyes in the polyester portion (68).

Softening Point of Polyester. Using HT-steaming instead of baking, reduces the fixation temperature (from 10 deg. C to 20 deg. C); therefore, disperse dyes of higher sublimation fastness, as required for durable-press finishes, are safely fixed at temperatures around 215 deg. C. This allows more tolerance by not operating close to the softening point of polyester fabrics (about 230 deg. C). Other advantages of operating below the softening point of polyester are improved uniformity and reproducibility (39, 68, 82).

Production. During HT-steaming, the fibers are always heated to

100 deg. C for a certain period of time before further drying occurs; whereas in baking, the cloth temperature at the dye fixation stage varies depending upon the humidity of the drying unit. Therefore, more reproducibility prevails in HT-steaming (82).

By using superheated steam thermofixation it is possible to increase the rate of production, reduce the power consumption, and occupy less space in the dye house (69).

Drying. There is no advantage in using the HT-steaming process for drying polyester simultaneously with disperse dye fixation, since dye fixation and diffusion do not occur under the drying conditions, but this process might be more advantageous for the fixation of reactive dyes in the cellulosic portion of the blend (82). Nevertheless, superheated steam possesses excellent drying properties (2, 43).

Equipment

Padders. It is advantageous to use padders that can provide more control of the processed materials. For yarns, padders composed of a lower steel roller and a heavy duty rubber roller on top are recommended. For fabrics, padders are equipped with air to control the amount of pressure required for each side and oil pressure for the center; resulting in a uniform wet-out of the fabric across the width and easy control of side to side and side to center shading. Migration during drying is also decreased because of the low pick-up that can be obtained using these padders (77).

Intermediate Drying. Intermediate drying of the padded goods is usually performed in two steps as follows: a rapid predrying with infrared radiation, which minimizes the particulate dye migration and brings down in a relatively short time the moisture content of the material to about 25%, then, complete drying and gradual heating of the goods is achieved by driving the cloth over heated cans (77).

For hot air thermofixation, the temperature of the goods entering the baking unit should be as high as possible to drive out moisture from the material and ensure the absence of water vapor in the unit (77). Whereas in superheated steam thermofixation there is no need to completely dry the cloth or heat it up, on the contrary, some residual moisture is desirable (68).

Thermofixation. The baking units are either gas fired hot air ovens, or semi-contact units. In the former, the unit is gas fired on the entrance with fans that force the flue through ducts that run the length of the unit at the bottom. Semi-contact units are also gas fired, however, this type has several large gas heated cylinders that the fabric passes over, which results in a decrease in the fixation time (77).

In steamers, large volumetric flow rates of superheated steam at higher temperatures than necessary are normally consumed; to compensate for the heat loss to the surrounding and prevent condensation on the inside walls of the steaming chamber, which can cause water drip spots on the processed material. Modern steamers now used in industry contain open live steam lines and closed

coil lines. The steamer side walls and ceiling are well insulated and maintained at a higher temperature than that of the steaming chamber. This is done by allowing the superheated steam, at a higher temperature, to run in the side walls and ceiling through closed coil lines before emerging out from open live steam lines to the steaming chamber at the required temperature. This has been found to reduce the steam consumption to about one third of that required without circulation (75, 77). All steamers of this type contain a water seal at the exit end, which prevents loss of steam, in addition to a continuous overflow of cold water, which eliminates dyestuff build up in the seal (77).

Continuous HT-steaming of yarns is done by using endless conveyor belts on which smooth winding up of yarn layers are deposited. A new phase of development was introduced with the cycloid deposition technique in the early seventies. The latest development has been made by using an endless converging conveyor that transports parallel wound yarns through the steam chamber for fixation (94).

Proper ventilation of the thermofixation unit is necessary to minimize the disperse dye precipitation on the equipment. The precipitated disperse dye can sublime in a latter time and be fixed on polyester; resulting in nonuniform dyeings (98).

CHAPTER III

EXPERIMENT DESIGN

Introduction

Continuous dyeing of the polyester-cotton blend is investigated. This is done by processing simultaneously three yarns of different compositions, namely, 100% polyester, 50%-50% polyester-cotton, and 100% cotton. The dyeing process consists of padding the dyeing liquor onto the cleansed yarns, then, fixing the dye into the fibers with superheated steam, and continuously collecting the processed yarns with a take-up system. Manual washing of the processed yarns is performed as soon as possible in order to avoid further fixation of the unfixed dye molecules.

The yarns are dyed with a disperse dye and a disperse-reactive dye mixture under different pH conditions. In addition, a reactive dye is applied to test its inactivity on the polyester fibers under the operating conditions and to evaluate the effectiveness of the washing process in removing the unfixed reactive dye, which presence is undesirable during the disperse dye extraction from the yarns that have been dyed with disperse-reactive dye mixtures. The dyeing behavior at different temperatures above 200 deg. C and near the melting point of polyester (about 260 deg. C) at varying residence times is explored. Fixation of the disperse dye is determined in each case by solvent extraction of

the dye with N, N-dimethylformamide (DMF) and spectrophotometric analysis of the extract to estimate the dye concentration in the extract. The amount of disperse dye is calculated in grams of dye per 100 grams of fiber for each sample.

Yarns Structure and Specifications

The investigated yarns are of three different compositions; 100% polyester, 50%-50% polyester-cotton blend, and 100% cotton. Upland cotton fibers varying in length from 2.54 cm (1.0 in.) to 3.18 cm (1.25 in.) and of an average diameter of $16.9\ \mu$ (1/1500 in.) are processed to produce the cotton yarn. The polyester yarn is made of Blue C Polyester fibers (Monsanto Textile Company) in the staple form possessing similar dimensions to that of the cotton fibers, namely, the staple fiber length varies like that of cotton and the fiber linear density is 3.0 denier, which assumes a fiber diameter of $17.5\ \mu$ (1/1450 in.). In addition, the polyester fibers are semi-dull and optically brightened. The blending on the drawing frame method is used to produce the polyester-cotton blended yarn.

Specifications of the yarns are as follows: simple single yarns, the yarn number (count) is according to the cotton system 20's (20 x 840 yards of yarn weighs one pound), and 20 tpi (20 twists per inch of yarn) with Z-twist, that is, the individual fibers are twisted in the counterclockwise direction during the yarn formation.

Yarns Preparation for Dyeing

The three types of yarns are equally treated in a solution containing sodium carbonate, 4% o.w.f. (this concentration unit stands for: on weight of fabric, or material to be wet treated), and Santomerse 85 (Monsanto Chemical Co.), 2% o.w.f., at 96 deg. C and under an average pressure of 2 atm (30 p.s.i.) for a period of two hours.

Before scouring, an appropriate amount of the yarn (weighing about 450 g or 1 lb.) is wound from the cone onto cylindrical perforated stainless steel dye tubes, and loaded in the single package machine tank (The Morton System, Model 72-148, Morton Machine Works, Inc.). The scouring solution is alternately circulated from out-to-in and in-to-out the package of yarn ; adjustment of the control is made to allow 3 min before the flow direction is automatically reversed. In addition, the heating of the circulating solution is programmed so that the temperature is gradually raised from room temperature at a rate of 1.7 deg. C/min (3 deg. F/min) to 96 deg. C , the temperature then remains at this level for two hours. This is followed by a thorough washing with cold water, spin drying, and finally drying in a hot air circulation oven (Isotemp Oven, Model 350, Fisher Scientific Co.) at 60 deg. C for four hours. The yarn is then conditioned at 65% relative humidity and 20 deg. C for 48 hr before being rewound on cones; ready for dyeing.

Santomerse 85 is an anionic surfactant that acts as a detergent and wetting agent; the concentration of the active ingredient, dodecylbenzene sodium sulfo-

nate, on a dry basis is 85%. Sodium carbonate is added as a builder in order to increase the detergency efficiency as well as to saponify oils, waxes, and other fiber surface dressings that interfere with dyeing.

Padding Liquor Formulation

The disperse and reactive commercial dyes investigated are Resolin Blue FBL (C.I. Disperse Blue 56, 63285) and Levafix Blue P-RA (C.I. Reactive Blue 104) respectively, both manufactured by the Verona Dyestuffs Company. The dyeing ingredient in the disperse dye is 1,5-diamino-4,8-dihydroxy-monochloro-anthraquinone, in addition to other necessary auxiliaries as dispersing agents and surfactants. Similarly, the reactive system in the reactive dye is 2,4-difluoro-5-chloro-pyrimidine (FCP) plus other additives.

Distilled water and the disperse dye are the only components forming the padding liquor for dyeing the polyester fibers by the HT-steaming process. A high disperse dye concentration of 50 g/l. is chosen to eliminate the effect of dye concentration on fixation.

A bath composed of 50 g/l. reactive dye, 20 g/l. sodium bicarbonate and varying amounts of monosodium phosphate and disodium phosphate to control the pH value, is prepared for the dyeing of the cotton fibers. A Corning pH meter (Model 12, Corning Scientific Instruments Co.) is used to determine the pH values in the dyeing solutions.

Preparation of the disperse-reactive dye bath is made at room temperature by dissolving separately the reactive dye, sodium bicarbonate, and the

disperse dye in small amounts of distilled water. The alkali solution is added to that of the reactive dye, which is then combined with the disperse dye solution. Then, equal weights of monosodium phosphate and disodium phosphate are gradually added to and dissolved in the final solution until the required pH value is reached.

For preparing 100 cu.cm of the disperse-reactive dye liquor, 5 g of each dye is dissolved separately in 30 cu.cm of distilled water and 1 g of sodium bicarbonate in 10 cu.cm of water. The solution is made up as described above and then water is added in order to bring the solution to its final volume, namely, 100 cu.cm. The phosphate salts are finally added to obtain the required pH value. It is important to keep in mind that the activity of these solutions is limited to a few hours; therefore, they are prepared at the last moment before starting the dyeing operation.

Equipment Design

Equipment are designed for the continuous dyeing of the yarns by the one bath, one pass dyeing method, including superheated steam thermofixation of the dyes.

Boiler

The boiler (see Figure 1 in Appendix C) consists of a horizontally erected cylindrical steel vessel, 30.5 cm (1 ft) in diameter and 91.4 cm (3 ft) long. Steam emerges out from a pipe that is 5.1 cm (2 in.) in diameter and 61 cm (2 ft) long and is situated on top and aside of the vessel; this is designed to

prevent water droplet entrainment in the superheating section. At the other side and on top of the boiler, a 10.2 cm (4 in.) flange is covered with a plate to which two pipes, 1.3 cm (0.5 in.) in diameter and 30.5 cm (1 ft) long, are connected; one pipe ending with a pressure gage and the other with a globe valve followed by a nozzle that is used as a water feed line as well as a steam outlet when necessary during the course of operation. A water level indicator is fitted to the end of the cylindrical vessel and at the opposite side of the steamer. Four gas burners are located underneath the vessel, which provide the heat energy essential for the steam generation.

It is important to treat the municipal water before feeding it to the boiler in order to prevent scale formation and the concentration build up of mineral salts in the boiling water, which result in inefficient heat transfer, hot spots formation, surface distortions, increase in the water boiling point, corrosion, water foaming and entrainment, and in extreme cases, flooding, or even explosion that is due to the instantaneous contacting of water with a red-hot spot of the vessel, this happens when the scale covering the hot spot suddenly peels off. In this research work, distilled water was available and has been used for the steam generation.

Superheater

Superheating the steam actually starts at the steam outlet from the boiler (see Figures 1 and 2 in Appendix C), through the 5.1 cm (2 in.) in diameter pipe, with five electrical heating coils (H1, H2, H3, H4, and H5). Further super-

heating is performed in a 2.54 cm (1 in.) in diameter and 122 cm (4 ft) long stainless steel piping before superheated steam is injected from the upper end of the steamer. The heating duty is achieved by seven electric coils (H6, H7, H8, H9, H10, H11, and H12). The superheating section branches to a 122 cm (4 ft) long pipe that provides steam for the lower end of the steamer; seven more heating coils (H13, H14, H15, H16, H17, H18, and H19) compensate for any heat loss to the surrounding. The end of this connection pipe is also fitted with a globe valve joined to a nozzle and a rubber hose in order to drain out any condensed steam from the system.

The electric resistance heating wire (insulated Chromel A wire, 22 gauge, Fisher Scientific Co.) is wrapped over a primary layer of fiber glass tape that covers the pipe to ensure a good electrical insulation. The heating coils are insulated from the surrounding with layers of asbestos tape. Each coil is about 10 m (33 ft) long and can provide a maximum power of 400 W when the applied potential is 115 V.

Steamer

The steamer (see Figures 2 and 4 in Appendix C) is composed of a vertical stainless steel pipe of 2.54 cm (1 in.) internal diameter and 152.5 cm (5 ft) long. Steam is injected from both ends of the steamer by means of two steam distributors. The steam distributor is made up of a main circular conduit, of 15.2 cm (6 in.) outside diameter, with a square cross section, 3.8 cm by 3.8 cm (1.5 in. by 1.5 in.), that is concentric with the steamer pipe. Four tubes, 0.32 cm

(0.125 in.) in diameter and 10.2 cm (4 in.) in length, branch off from the main conduit such that they join the steamer pipe at an angle of 23 deg.; thereby, steam from the upper distributor is injected downwards, whereas the steam from the lower distributor is injected upwards. Therefore, practically no air enters the system, since the steam is equally evolved at about 10 m/sec (33 ft/sec) from both ends of the steamer. Each steam distributor is connected to a gate valve in order to control the steam flow.

Twelve heating coils surround the steamer pipe and the distributors, as shown from Figure 2 in Appendix C, to compensate for any heat loss to the surrounding. In addition, the whole steamer is enclosed and insulated with fiber glass, except at the steam outlets where openings with some clearance are designed to avoid overheating.

Temperature Control and Measurement

Figure 3 in Appendix C shows the five heating sections (S1, S2, S3, S4, and S5) and their connection to the control units, the five variable transformers can be seen in Figure 5. The temperature of the superheated steam in the steamer is manually controlled by five variable transformers (V1, V2, V3, V4, and V5), the voltage input is 120 V (60 Hz) and the voltage output can be varied from 0 V to 120 V, in addition, the maximum amperage to be regulated by V1 is 10 A, V2 and V3 is 25 A each, while V4 and V5 are not expected to control more than 15 A each, this occurs when the transformer output is 120 V.

The first and second heating sections (S1 and S2) perform the major super-

heating duty, whereas the three other sections (S3, S4, and S5) are confined to heat compensation. It has been found that if the compensation sections are loaded to perform any important steam superheating it becomes very difficult to obtain a uniform temperature profile all along the steamer, even if the steam flows at similar rates from both ends of the steaming pipe.

Adjustment of the variable transformers to produce a required temperature in the steamer is strongly dependent on the ambient temperature as well as the rate of steam generation, which is essentially controlled by the gas burners. Nevertheless, primary adjustments are first made by a trial and error process until the required temperature prevails uniformly throughout the steamer; and, minor adjustments are usually necessary in the course of each run.

Measurement of the superheated steam temperature at both ends of the steamer is made by means of a general laboratory mercury thermometer (76 MM IMM, 14-985-5 G, Fisher Scientific Co.). In this thermometer, the space over the mercury column is filled with nitrogen, the temperature range is from -10 deg. C to 400 deg. C, graduated by 2 deg. C divisions, the stem length is 400 mm, and the graduation is calibrated at 76 mm immersion while the stem is in the vertical position; with the mercury bulb directed downwards.

The thermometer meets the Scientific Apparatus Makers Association (SAMA) specifications, which are available in the SAMA standard bulletin number CP 30 for general purpose glass laboratory thermometers. The recommended tolerance limits for this thermometer are 2.5 deg. C for the temperature

scale extending from -10 deg. C to 300 deg. C and 5 deg. C tolerance for temperatures above 300 deg. C. Nevertheless, by calibrating the thermometer against an iron-constantan thermocouple no temperature difference could be observed at 0 deg. C and 100 deg. C, however, at 200 deg. C the thermometer reading is at about 201.5 deg. C. The thermocouple junction temperature is determined from the "Modified 1913 Calibration Table", which is based on the "International Temperature Scale of 1948." A precision potentiometer (8686 Millivolt Potentiometer, Leeds and Northrup Co.) is used to measure the electromotive force generated across the thermocouple terminals. Figure 6 in Appendix C shows the thermometer calibration plot, which has been approximated to a straight line.

A glass mercury thermometer will exhibit slight differences in the observed temperature according to the varying extents of the stem immersion, standing position, rate of heat transfer, and previous heat subjection history. However, the most important source of error is caused by the thermometer stem immersing other than specified; equations correcting for this type of error can be empirically found, or usage can be made of general equations provided by the thermometer manufacturer. Another source of error is the observer himself--an unpredictable source of error.

Nonetheless, the thermometer had been tested in boiling distilled water under total and partial immersion conditions; and no temperature difference was discerned. This might be due to the 2 deg. C scale division, which does not

allow precise temperature reading. Similarly, in melting ice no temperature change was noticed whatever the immersion or standing positions were. Therefore, no provision is made to correct for the stem emergent or standing position and it is assumed that these sources of error are of minor importance and would cause unnecessary complications.

As soon as the cold thermometer is immersed in the steamer, steam condensation occurs on the thermometer stem; a few minutes might be necessary until the condensed water evaporates and the maximum temperature is reached. The temperature is measured at different distances and from both sides of the steamer; in order to ensure a relatively uniform temperature profile throughout the whole length of the steaming pipe.

Furthermore, the temperature of the superheated steam flow that evolves out of the steamer drops very sharply and mixes instantaneously with the surrounding air without condensing on the equipment. Therefore, it is assumed that the yarn passage through this portion of the steam-flow possesses a negligible effect on the total extent of dye fixation; and the actual steaming length can be fairly approximated by the length of the steaming pipe.

Padder and Residence Time Control

The yarns are pulled from the cones by the rollers of the padding unit (manufactured by H. W. Butterworth and Sons Co.), as can be seen from Figures 4 and 5 in Appendix C, and are driven first under a glass rod that is immersed in a glass trough having a semi-circular cross section, 3.18 cm (1.25 in.) in

diameter and 25.4 cm (10 in.) long. At the beginning of each run, the padding liquor volume is 70 cu.cm; such that the solution totally covers the driving glass rod. Nevertheless, more padding liquor is added during the course of operation to compensate for the liquor consumption, especially at higher padding speeds. A considerable amount of the liquor is wasted on the padding rollers; the dripping solution cannot be collected in the original trough in order to maintain a constant padding bath composition.

After imbibition, the yarns are driven through two rollers, 8.4 cm (3.3 in.) in diameter each, coated with a layer of polypropylene. The pressure applied on the rollers is 2.7 atm (37 p.s.i.), however, this does not necessarily mean that the pressure on the yarns is 2.7 atm during operation.

When the padder is at rest, the pinch points resulting from nipping the yarns between the two rollers cause nonuniformities in the stress distribution along the surface of contact between the two cylinders; the pinch points form centers of stress concentration that produce further deformation of the polypropylene layer. Ideally, if the yarn were a steel rod, the two squeezing surfaces of the rollers will be shaped into two semi-circles. But actually what happens is that both the yarn and roller surfaces are deformed at their point of contact until a more uniform stress distribution pattern is established.

As the rollers start rotating, pulling the yarns from one side and delivering them to the other side, the deformation created at the pinch points on the roller surfaces do not recover immediately; therefore, after the first revo-

lution a narrow and shallow groove starts shaping up on the polypropylene layer. Because the polypropylene is not allowed total recovery, whereas the yarns are continuously fed through the same pinch points, the initiated groove on the periphery of the rollers gradually grows until a state of dynamic equilibrium is reached, which is partially dependent on the yarn structure, speed of rotation, and pressure applied. Therefore, the pressure on the yarns would be lower than expected, particularly at higher speeds.

During operation, the cotton yarn and the polyester yarn run at both sides between the padding rollers, while the polyester-cotton blended yarn is driven in the middle. The pressure on the rollers is controlled by compressed air at both ends of the driving shaft of the lower roller, and since the length of the rollers is about 30.5 cm (1 ft), no pressure control is provided for the middle of the padder.

At a speed of about 5.3 r.p.m., the average wet pick-up for the polyester yarn, the cotton yarn, and the polyester-cotton blended yarn is 78%, 106%, and 154% respectively. The reason for which the cotton yarn picks up more liquor after padding than the polyester yarn is self explanatory: polyester is hydrophobic and cotton is hydrophilic. Explaining the high pick-up of the blended yarn is more difficult, however, it might be that because of the coring effect, the polyester fibers--with their uniform circular cross section--located in the core of the yarn offer some resistance to the flattening out of the whole yarn structure; thereby the cotton fibers, which are mostly situated at the yarn pe-

riphery, are spared from being squeezed out as in the case of a 100% cotton yarn.

The motor driving the padding rollers rotates at a constant speed of 1200 r.p.m. (1.5 hp) and is coupled to two reduction gear boxes, with 1:15 gear ratio each, thereby, the speed output reduces to 5.3 r.p.m. In order to ensure a positive drive of the rollers without slippage, as in the case of a belt driving a pulley, a sprocket (20 teeth and $\frac{3}{8}$ in. pitch) is fixed on the output shaft and a chain transfers the motion to another sprocket mounted on the driving roller shaft.

Two different residence times are investigated, namely, 64.7 sec and 21.6 sec. If both the prime mover sprocket and the driving roller sprocket have the same number of teeth, the speed conveyed to the padding rollers will remain unchanged, that is, 5.3 r.p.m., which produces a linear speed of 137.8 cm/min for the processed yarns (this results from multiplying the roller perimeter, 26.5 cm, by the rotational speed, 5.3 r.p.m.). Since the actual steaming pipe length is 152.4 cm (5 ft), thus the time taken by any yarn segment to travel through the steamer is 64.7 sec (the result of dividing the steamer pipe length, 152.4 cm, by the linear speed of the yarns, 137.8 cm/min). Tripling the yarn linear speed can be done by replacing the prime mover sprocket by another sprocket with three times more teeth (60 teeth); thereby, resulting in a residence time that is one third of the original, i.e., 21.6 sec ($64.7/3$ sec).

Yarns Take-Up

The take-up system (see Figures 4 and 5 in Appendix C) is designed to collect the processed yarns at the same speed they are fed by the padding rollers. A variable speed motor rotates a shaft on which three bobbins are mounted. The bobbins are made up from cylindrical perforated stainless steel dye tubes with plastic ends. Furthermore, available plastic partition rings can be fixed on a dye tube; thereby, the collection of the three yarns can be made on a single bobbin.

No device is provided to either distribute uniformly and synchronously the yarns on the bobbins, or to adjust the motor speed to correct for the variation in the winding diameter with time--the take-up speed is directly proportional to the winding diameter. Therefore, frequent manual interference is necessary to arrange the windings and readjust the motor speed.

Yarns Driving

Driving the yarns (see Figures 7, 8, and 9 in Appendix C) from the padding rollers to the steamer and finally to the take-up system requires the use of guides that would provide the minimum amount of friction on the yarns. Whenever a yarn changes direction along its path, a small and light pulley, which rotates freely around a wire, is used for the guidance. The friction between the yarn and the pulley channel, which is function of the tension applied on the yarn and the surface characteristic properties, drives the pulley to rotate around the holding wire and against the frictional force between

the internal surface of the pulley hole and the holding wire, which is considerably less than the friction developed by the sliding of a yarn over a glass rod, especially when the yarn is wet with the padding liquor.

On the other hand, the turbulent superheated steam flow in the steaming pipe might occasionally agitate the processed yarns, which move in the upwards direction inside the pipe, causing the yarns to sway despite the tension applied; thereby, getting in contact with each other, or with the hot wall of the steamer, which is at a higher temperature than the flowing steam. Therefore, regular ceramic guides are fixed at each end of the steamer in order to straighten up the yarn path, so that, under stationary conditions the yarn passes through the middle of the guide hole, and during operation, the yarn occasionally touches the guide with practically no persistent friction resulting.

It is essential to ensure a continuous and uniform feed of yarns to the steamer. However, no automatically controlled synchronization exists between the rotation of the padding rollers and the take-up bobbins. In addition, due to the process conditions, the yarns might be subject to minor dimensional changes which are dependent on the yarn composition as well as contingent nonuniformities in the yarn structure throughout its length. Hence a tensioning system (see Figures 7 and 9 in Appendix C) is included, which allows any irregularity in the yarn feed to be embraced in a length of yarn that is kept stretched by means of a hooked weight connected to a pulley that is suspended on the yarn; forming the tip of a V-shaped path.

For instance, if the yarn take-up accelerates, due to an increase in the winding diameter on the bobbins, the hooked weight will move upwards; thereupon indicating that the speed of the driving motor must be readjusted until the weight reaches an arbitrary lower height. At the same time, it may be also necessary to shift the winding position of the other two yarns; so that the take-up of all the three yarns becomes the same.

The pending weight in the tensioning system should produce a strong enough force to pull off the wet yarn that is driven out of the padding rollers and to prevent it from adhering any further to the moving roller surface, which is covered with the viscous dyeing liquor. Otherwise, the yarn will be pulled off out of the steamer and wound up around the padding roller instead of the take-up bobbins; leading to the yarn breakage. In addition, the pending weight should keep the three yarns as straight as possible during their passage into the steamer in order to avoid the yarns entanglement, which is strongly enhanced by the electrostatic attraction and the closeness of the yarns in the steaming pipe. Entanglement of the yarns in the steamer causes breakage, which necessitates a temporary shutdown for passing the yarns back through the steaming pipe.

It has been found--from experience--that at the beginning of operation a heavier weight is needed for tensioning, e.g. 50 g, however, after that steam reaches a higher level of superheat, the weight can be reduced, e.g. 26 g . This is due to the steam condensation on some of the guiding pulleys during the

early stages of operation; thereby rendering their rotation more difficult. Figure 10 in Appendix C shows the average tension forces distribution along a driven yarn during steady operating conditions.

Start Up

First, the yarns are passed through the guides and an appropriate weight is used for the tensioning. A special yarn holder (see Figure 11 in Appendix C) is designed to lead the yarns through the steaming pipe. It is recommended at this stage to check on the yarns driving motion; by operating the padding rollers and the take-up system for a short period of time.

The boiler is then filled with distilled water and the gas burners are lit up. It takes about 45 min for the steam to begin evolving out of the steamer. The variable transformers can be operated and set to low voltage values 15 min before the steam generation; to warm up the different heating sections. As the steam starts evolving at similar rates from both ends of the steamer, the voltage of each heating section is gradually increased to its ultimate value.

When the steam generation initiates, the degree of superheating is low and the steam is highly susceptible to condensation; some condensed water forms at both ends of the steamer. However, after a few minutes the steam rate increases, higher superheating is produced, and the leaving steam is mixed with the surrounding atmosphere without condensing on any part of the equipment. The steam temperature starts rising slowly until a quasi-steady state is reached, and readjustment of the variable transformers might be necessary until the tem-

perature of the superheated steam all along the steamer becomes the same.

After filling the padding trough with the dyeing liquor, the yarns are set to motion. This can be done at any time during the steam evolution, however, to decrease the chemicals and yarns consumption, it is advantageous to postpone this step as much as possible. Nevertheless, the yarns should be padded and steamed for at least half an hour before the required temperature conditions are attained and sampling starts, this is important in order to reach steady padding and steaming conditions of the yarns.

Shutdown

A temporary shutdown is necessary in order to reset the yarns in motion after any yarn breakage, or to refill the boiler with water. This is simply done by turning off the gas burners, then, gradually lowering down the variable transformers. However, it is safer to wait for a few more minutes until all the steam is released, before supplying the boiler with water.

Ordinary shutdown is made by first cutting off the gas burners, then gradually turning out the variable transformers. Finally, the padder and take-up motors are shut off. It is recommended to wash out the padding rollers as soon as possible and let them freely run--with no yarns--for a period of time until the marks left by the yarns disappear and the polypropylene layer on the rollers even up.

Sampling of Yarns

With proper adjustment of the variable transformers, a quasi-steady state

that lasts for about one hour can be reached. The sampling is made for a period of 30 min under the required conditions of temperature, residence time, and padding liquor composition.

As soon as the expected temperature conditions are obtained, three bands of paper are applied over the three yarn windings around the take-up bobbins; thereby, isolating the yarn samples. After 30 min, three other paper bands are applied, and the process is shutdown. The samples (usually weighting less than 3 g each) are then readily labelled, removed from the bobbins, and washed off in order to prevent any further dye fixation from occurring.

Washing Off the Unfixed Dye

Disperse Dye

Each yarn sample is first thoroughly rinsed with cold water to remove as much of the unfixed dye as possible. Afterwards, the sample is treated with a 75% methanol and 25% water solution at 0 deg. C, the water diluted methanol solution at the low temperature dissolves the unfixed dye without stripping the fixed dye molecules from the fibers. Every sample is well stirred for 5 min into 30 cu.cm of the alcoholic solution in a 100 cu.cm capacity beaker that is immersed in an ice bath. This treatment is successively repeated with fresh amounts of the methanol solution until no more dye comes out of the sample. The yarn samples are then rinsed with water and allowed to dry at room temperature.

Polyester yarns are readily cleaned after about seven treatments, whereas

the cotton yarns (or polyester-cotton blended yarns) might need as many as thirty successive treatments, or more, to produce a satisfactory removal of the unfixed dye.

Reactive Dye

Removal of the unfixed reactive dye from the yarns is initiated by a thorough rinsing with hot water. Each sample is then well stirred during 5 min and at 95 deg. C in 200 cu.cm of a solution containing 5 g/l. Santomerse 85 (anionic detergent, dodecylbenzene sodium sulfonate) and 10 g/l. sodium carbonate. The sample is then removed to a similar solution that is at about 50 deg. C and stirring is continued for twenty more minutes. This is followed by a thorough rinsing in cold water and then hot water. Finally, the yarns are dried at room temperature.

The reactive dye used forms with the cellulosic fiber an ester bond, which is resistant to the alkaline conditions prevailing during the washing process. On the other hand, the unfixed reactive dye hydrolysis is catalyzed under alkaline conditions, however, the unfixed dye--even when hydrolysed--exhibits a slight affinity for cotton. Hence, the primary wet treatment at 95 deg. C enhances the hydrolysis and mobility of the unfixed dye molecules, in addition, it increases the solubility and penetration of the detergent. During the secondary treatment, at 50 deg. C, the detergent molecules assemble around the unfixed dye, drive it out of the yarn, and maintain it in the solution, at the same time, sodium carbonate works as a builder; increasing the detergent efficiency.

Disperse and Reactive Dyes

Washing off the yarn samples that have been dyed with disperse-reactive dye systems is done by first removing the unfixed reactive dye then the disperse dye as it is described above. Under these conditions, the cotton yarn is more easily stripped of the unfixed disperse dye embedded in the cellulosic structure; about twenty treatments with the methanol solution become necessary to bring about satisfactory cleaning.

Disperse Dye Extraction

The extraction of the disperse dye is carried out on an appropriate size (about 1 g) of the original sample; thereby, the extraction process becomes handy and no unnecessary amounts of chemicals are consumed. The weight of the sample to be extracted is first determined on a dry basis. About 1 g of each sample is dried during two hours in the hot air circulation oven (Isotemp Oven). After drying, the sample is rapidly placed on the balance cup (Mettler P 1200, Mettler Instrument Co.) and its dry basis weight is measured.

The disperse dye is extracted from the fibers by DMF (N,N-dimethylformamide, D-119-S, Fisher Scientific Co.) at 100 deg. C. Each sample is stirred for 5 min into 20 cu.cm of DMF contained in a 120 cu.cm capacity Erlenmeyer flask, which is maintained at 100 deg. C by immersion in a boiling water bath. This extraction step is successively repeated with fresh amounts of the solvent until no further disperse dye can be noticed in the extract. The solvent consumed during the extraction of the sample is collected, and the extract total

volume is determined.

Satisfactory dye removal from the fibers can be achieved after an average of seven extraction steps. However, due to the low affinity of disperse dyes for cellulose, the dye is more easily extracted from the cotton fibers. On the other hand, with appropriate removal of the unfixed reactive dye, no reactive dye--either fixed, or unfixed--comes out of a sample that has been dyed with a disperse-reactive dye mixture during the DMF extraction. This has been checked by trying to extract the dye from yarn samples that had been dyed with the reactive dye only; and no coloration of the DMF was observed.

Dye Concentration Measurement

Determination of the dye concentration in the solvent extract is made by measuring the light absorption at the wave length at which maximum absorption occurs (maximum absorption wave length). According to Beer's Law: the light absorbed by a solution is proportional to the number of molecules of the absorbing substance through which the light passes. The law does not hold in case where the dye molecules associate; however, in a certain concentration range, the relation between the dye concentration and the light absorption can be fairly approximated to a straight line, as in Figure 15 in Appendix C.

A Baush and Lomb spectrophotometer (Spectronic 70, with multiple sample compartment, Model 33-30-02) is used to measure the light absorption of the dye solutions at different wave lengths (dye solution spectrum). White light (a light exhibiting similar intensities at different wave lengths) from a

tungsten lamp is passed through a diffraction grating to produce a light spectrum. By suitable rotation of the grating an emergent beam of predetermined wave length can be obtained. Light of known wave length produced in this manner is passed successively through a reference cell and the sample cell. The emergent beam is caused to fall on a photoelectric cell that generates a corresponding electric signal that is amplified and conducted to a galvanometer, thereby, the electrical current is converted to a mechanical motion in which the galvanometer needle gyrates on a graduated dial, which indicates on a logarithmic scale the light absorption (from 0.0 to 2.0 absorbance) and on a linear scale the equivalent percent light transmittance (from 0.0 to 100% transmittance). The reference cell is assumed a value of 0 absorbance (or 100% transmittance). This is done by adjusting a variable resistance that controls the intensity of the current driving the needle. The sample cell absorbance is then measured, and the dye concentration is determined from a previously plotted chart, which relates the dye concentration versus light absorption, or directly from the proportionality constant between the two variables when a straight line relation prevails.

Values in Tables 7 and 8 are plotted in Figures 12 to 14, in Appendix C, these show the light absorption variation with wave length for the disperse, and reactive dye at different concentrations when dissolved in water, and DMF.

Sufficient time, e.g. one hour, should be allowed to elapse before starting the spectrophotometric measurements to permit the instrument electronic

components to reach steady state operating conditions. In addition, it is necessary that a set of integrated experimental measurements be carried out uninterruptedly. For example, when a comparison is made between the light spectra of two differently concentrated disperse dye solutions in DMF, it is unlikely that their maximum light absorption wave length will be the same if the spectrophotometer is turned off after determining the spectrum of one solution, and then, measurements for the other solution are pursued at a later time; a few nanometers (nm) of difference, e.g. 5 nm, might be observed. Nevertheless, if the light spectra of the dye solutions are measured successively and repeatedly at different extended time intervals, the light absorption difference between each pair of spectra measured successively remains practically unchanged, although the maximum absorption wave length for each of these pairs of spectra might not be the same. Consequently, a proportionality constant between the dye concentration and the light absorption does not vary as long as the dye solution absorption is measured at the maximum absorption wave length, which must be redetermined each time measurements are made.

The disperse dye concentration in DMF should be regarded as nominal, since this solvent does not dissolve all the components incorporated in the commercial disperse dye, although the reactive dye is more soluble in DMF. About 35%, by weight, of the disperse dye constituents are soluble in DMF, and the remaining undissolved 65% are basically dispersing agents, which possess a yellowish green color and are rather water soluble. This explains the different light

absorption characteristics of the disperse dye water solutions, especially in the yellow region (from 400 nm to 420 nm) of the spectra in Figures 13 and 14 in Appendix C. However, the reported concentrations are an indication of the total amount of the commercial disperse dye necessary to obtain dye solutions exhibiting the light absorption spectra shown in Figures 12 to 15 in Appendix C.

Leaching can be used to estimate the commercial disperse dye contents that are insoluble in DMF. A filter paper (prepleating folded paper with medium porosity, Grade 802, Reeve-Angel Co.) is first cut to fit a Buchner type funnel, and then weighted. The funnel is fitted onto a filtering flask, which is connected to a filter pump, and a known weight of the dye is placed on the filter paper. Afterwards, the percolating liquid (DMF) is poured over the dye while continuously stirring the accumulated solution in the funnel. This is continued until the filtrate dripping from the funnel becomes clear. After leaching, the filter paper, with the remaining residues, is placed on a watch glass and dried in the circulating air oven (Isotemp Oven) at 170 deg. C, above the boiling point of DMF (153 deg. C), for two hours. Then, the filter paper is repeatedly weighted at different time intervals until the observed weight remains unchanged. This is due to the moisture absorption and reconditioning of the dried material; about eight hours might be necessary to reach an ultimate moisture regain of 4%.

CHAPTER IV

RESULTS AND DISCUSSIONS

Steaming Temperature Effects on Polyester Fibers

Introduction

It had been planned to investigate dye fixation temperatures above 200 deg. C and near the polyester fiber melting point, which is around 260 deg. C when measured in an air atmosphere using the hot plate method (Fisher-Johns Melting Point Apparatus, Fisher Scientific Co.). The tentative highest steaming temperature was to be 240 deg. C, which falls within the upper limit of the polyester softening temperature range (from 230 deg. C to 240 deg. C) determined from penetrometric measurements in air (70).

On the other hand, by referring to the literature (65) furnished by the dye manufacturer (see Figure 27 in Appendix D) it is found that at 220 deg. C (428 deg. F), which is the average temperature in the range to be explored, maximum fixation of the disperse dye (Resolin Blue FBL) on polyester is obtained at a residence time around 60 sec.

The manufacturer's data is provided for the processing of a 65%-35% polyester-cotton blended fabric that is first padded with the dyeing liquor, dried for one minute at 127 deg. C (260 deg. F) with an infrared drier, then the dye fixation takes place in a Benz thermosol unit by means of circulating hot

dry air. The dye fixation is determined by leaching out cotton in the blend with a cold 70% sulfuric acid solution. Then, from light reflectance measurements of the remaining dyed polyester skeleton and by considering the heaviest shade obtained to be 100% fixation, the relative percentage of fixation for the rest of the samples is evaluated (65).

Hence, it has been found convenient to start with a steaming residence time of 64.7 sec; considering the thermal properties of steam in conveying heat for drying and its advantageous dye fixation characteristics (39, 82), in addition to the availability of the necessary machine parts that can drive the padding rollers to feed the yarns at the equivalent linear speed (137.8 cm/min).

However, during the course of operation, the processed yarns would frequently break up whenever the steaming temperature is raised above 200 deg. C--leading to repeated shutdowns and rendering further yarn processing ungovernable, especially at 220 deg. C. Nevertheless, at 200 deg. C the dyeing operation proceeds continuously and smoothly with no casual yarn rupture.

Therefore, the investigated steaming temperature has been limited to 200 deg. C and the disperse dye fixation is determined for the polyester yarn, the polyester-cotton blended yarn, and the cotton yarn; under different padding liquor compositions, namely, disperse dye, disperse-reactive dye mixtures at pH values above and below 7pH, and reactive dye. Furthermore, the disperse dye fixation is determined at two different residence times, i.e., 64.7 sec and 21.6 sec.

Microscopic Analysis of the Ruptured Yarns

From a closer examination of the polyester yarn broken ends that had been steamed at 220 deg. C, it was possible to discern partial melting of the polyester fibers located at the yarn periphery as shown in Figures 21 and 22 in Appendix D. Other portions of the yarn exhibited fusion of individual fibers. This is clearly seen in Figures 17 to 19 in Appendix D. Thin points in the yarn would be more likely to initiate rupture.

The polyester yarn is always the first to break while the polyester-cotton blended yarn breaks next if it is left long enough stationary in the steamer, e.g. for a few minutes—depending on the steaming temperature. However, samples from the blended yarn taken at the same time as the polyester yarn breaks, exhibit similar fiber fusion as shown in Figure 20 in Appendix D.

Tensioning Weight Variation

The frequent polyester yarn rupture at higher steaming temperatures first suggested the possibility that the tension applied to the processed yarn might be excessive; thereby, accelerating the yarn rupture, particularly during the yarn passage through the superheated steam. At high enough steaming temperatures, e.g. 220 deg. C, partial melting of the fibers occurs and a tensile strength applied under these conditions might have an important contribution in driving the fibers and accordingly the yarn apart. Hence, the tensioning weight was reduced from 26 g to 15 g--jeopardizing the yarn motion smoothness (see Chapter III). But this did not affect the yarn rupture frequency at high steaming

temperatures above 200 deg. C. Further decrease in the tensioning weight to a few grams (5 g and then 2 g), which required frequent manual intervention in the yarn motion to ensure a continuous running, was fruitless. By finally increasing the tensioning weight to 80 g with no observable change, either worsening or bettering, in the yarn processing at the higher temperatures, it was concluded that the applied tension is immaterial to the yarn rupture under the operating conditions.

Steaming Residence Time Reduction

The following attempt was to cut down the yarn residence time in the steamer to one-third of the original (64.7 sec), i.e., 21.6 sec; in order to forestall total yarn melting, extension (or flowing), and separation at the rupture point. Nevertheless, the frequency of the yarn rupture *remained unchanged at high* steaming temperatures above 200 deg. C, especially at 220 deg. C, which renders further processing intolerable because of the continual yarn rupture. Although shorter residence times were not examined it is unlikely that yarns with a wet pick up varying from 78% to 154% will heat up to 220 deg. C in superheated steam in much less than 20 sec (39, 82).

Polyester Fiber Melting Point Determination Using the Hot Plate Method

In the hot plate method for determining the melting point of polyester fibers, the fiber sample is inserted between two micro cover glasses and placed on a heating aluminum stage that accommodates the mercury bulb of a specially designed thermometer (12-142 T Thermometer, Fisher Scientific Co.). When the

melting point is approached the fibers become transparent (collapse) and at the same time gradually lose shape by shrinking and forming separate liquid droplets that finally gather into a virtually transparent molten mass. The primary fiber shrinkage occurs because of the internal stresses induced during the fiber manufacture and processing.

For this specific measuring instrument (Fisher-Johns Melting Point Apparatus), depending on the sample size and rate of heating, a few seconds elapse before the collapsed fibers end up in a molten mass. For a 2.5 cm (1 in.) long polyester yarn sample that is heated at the rate of 1 deg. C/min at the proximity of the anticipated melting point, about 6 sec are necessary for the collapsed fibers to melt while the observed temperature remains unchanged. The rate of heating is regulated to 1 deg. C/min by adjusting the variable transformer incorporated in the apparatus. This is briefly how the polyester yarn melting occurs when the heat is applied to the yarn by conduction.

HT-Steaming Heat Transfer Mechanism

During steaming, heat is transferred to the polyester yarn by virtue of convection and radiation--although some heat is transported by conduction between the individual fibers in the yarn. The yarn heating process can be resolved into three different stages as follows: steam condensation and yarn heating to 100 deg. C, yarn drying at 100 deg. C, and yarn heating to the ambient superheated steam temperature.

Steam condenses on the padded cold yarn as it enters the steamer and

releases its latent heat to the yarn, the average heat transfer coefficient during this stage is estimated to be 4880 Kcal/hr/sq. m/deg. C (1000 Btu/hr/sq. ft/deg. F). This is an extremely rapid step that ends in less than one second. During the drying stage, water is evaporated from the yarn at an approximately constant temperature of 100 deg. C (212 deg. F), since the pressure in the steamer is about one atmosphere. This is the slowest yarn steaming phase, which lasts for approximately 15 sec (order of magnitude). After drying, the yarn temperature starts rising up by virtue of sensible heat transfer from the steam flow as well as by radiation from the steaming pipe wall. It takes roughly about five more seconds for the yarn to reach the ambient temperature (39).

It is conceivable that exact calculation of the yarn heating rate is not simple, since the padded yarn system varies in temperature and composition throughout its passage through the steamer, exothermic reactions take place, and the surface area of heat transfer is difficult to determine under these continuously varying conditions. In addition, there are temperature gradients across the yarn cross section, which are clearly manifested in Figures 21 and 22; where some of the polyester fibers are totally melted and spread over fused or intact fibers.

Further Experiments on Polyester Melting

The nature of the polyester yarn rupture during steaming does not allow a thorough examination of the broken yarn extremities (tips) cross section--because of the yarn end coiling up and entanglement after its rupture. Therefore,

further experimentation was effected in order to study the nature of the polyester yarn rupture during steaming around 220 deg. C.

An undyed polyester yarn about 30 cm (1 ft) long had been suspended stationary, but stretched with a 2 g weight, in the middle of the steamer. While the temperature was approaching 220 deg. C the yarn broke with a neck formation, this is clearly demonstrated in Figures 23 and 24 in Appendix D. From the yarn tip cross sectional view, it can be noticed that not all the individual fibers in the yarn melted, but some intact fiber ends can be observed into the yarn cavities; although each one of these individual fibers might have formed a neck before rupture. The neck tip sharpness--for either the whole yarn or individual fiber ends--could be an indication that practically no resistance is offered against the yarn flow under the prevailing conditions. This might also be interpreted as a ductile breakage due to creep at 220 deg. C under a 2 g load, whereas under the standard conditions (20 deg. C and 65% relative humidity) the yarn breaks under a load of about 770 g when the gage length is 25.4 cm (10 in.) and the yarn is subject to a constant extension rate of 12.7 cm/min (5 in./min); using an Instron tester.

Polyester fiber portions remaining without total melting in the yarn cavities are the result of their being shielded by the surrounding air and molten polymer; therefore, thermally isolated from the outside superheated steam. As the yarn begins flowing and the neck starts forming, the surrounding molten polymer layers become thinner; thereby, allowing more heat transfer to the

yarn interior and contributing to the shielded fibers gradual flow.

The following experiment had been done to ensure that total yarn melting and liquifaction occurs when ample time is given for the heat transfer throughout the yarn to take place. An undyed polyester yarn was attached at both ends to a wire ring periphery such that the yarn lies unstretched along the ring circular diameter (1.5 cm); the wire ring was held concentric with and in the middle of the steaming pipe. In addition, provision was made to prevent the ring from contacting the steamer wall. At different time intervals the ring would be brought out for examination. As the temperature was approaching 220 deg. C the yarn suddenly disappeared from the ring and traces of solidified molten polyester were observed at positions where the yarn had been attached. This could be interpreted as follows: around 220 deg. C the individual polyester fibers gradually melt, starting at the yarn surface, and the whole yarn is then transformed to a viscous liquid that loses its yarn shape and falls off by its own weight leaving traces in places where it was previously fixed. The polymer undergoes a drastic change in its mechanical properties that corresponds to a first order transition, since the yarn flowed under its own weight of 0.0007 g while the same yarn under the standard conditions breaks under a load of 770 g; as described previously.

Polyester Melting Dependence on Steaming Temperature

Reducing the tensioning weight on the polyester yarn forty folds, from 80 g to 2 g, and decreasing the steaming time to one third, from 61.7 sec to

21.6 sec, did not spare the yarn rupture at steaming temperatures as high as 220 deg. C and above 200 deg. C, e.g. 205 deg. C--although less frequently.

Hence, it is evident that the observed yarn rupture with the corresponding partial fiber melting is strongly temperature dependent rather than stress, which results from the yarn tensioning, or time dependent; under the steamer operating conditions.

In addition, the two experiments that had been carried out on unpadded polyester yarns might be an explanation for the tensioning weight insignificant effect on the yarn rupture at the higher steaming temperatures, since a 2.54 cm long polyester yarn subject to melting flows under its own weight (0.0007 g) while the lowest tensioning weight used is 2 g and the necessary weight to provide a smooth yarn processing is about 26 g.

From a closer observation of the melting process in the hot plate method, once the melting point is reached, a few more seconds are enough for the total yarn melting to occur. This elucidates the steaming time slight influence on the polyester yarn rupture at the higher steaming temperatures, since the shortest residence time is 21.4 sec, which probably includes enough time for a fiber to melt once the melting point is reached.

Critical Operating Conditions

Steaming for a residence time such that the polyester yarn is driven out of the steamer as soon as the yarn surface temperature raises to, say, 220 deg. C, is impractical, since the yarn has different structural nonuniformities through-

out its length, e.g. thin points in the yarn would require less time to heat up, in addition, even if the yarn were assumed perfectly uniform, the setting of operating conditions near critical phase transitions is undesirable, unless highly sophisticated automatic steam temperature control prevails, which might not be feasible. It is always advantageous to carry on continuous processes with some tolerance in the operating conditions; without affecting the reproducibility or the processed goods quality.

The reason for which it has been suggested--hypothetically--to drive out of the steamer the polyester yarn as soon as the yarn surface temperature reaches 220 deg. C, is that by the time the yarn core attains 220 deg. C, the superficial fibers may already be melting and further fiber melting propagation deeper in the yarn cross section should be avoided in order to prevent the yarn flowing or rupture.

Polymer Heterogeneity

Low molecular weight substances usually exhibit a sharp melting point. High molecular weight materials, like polymers, are composed of different chain length molecules that combine in varying structural configurations; three dimensional ordered crystallite regions, two dimensional ordered oriented regions, and less ordered amorphous regions. Sections of one chain molecule may frequently be involved in more than one configurational pattern. Most polymers exhibit a melting temperature range of about 10 deg. C that generally terminates abruptly at a more defined temperature (70).

Polymers melting initiates when the heat energy provides the molecular chains with enough thermal agitation that liberates the chains from the crystallites to the amorphous regions. Less perfect and less stable crystallites melt first and more stable ones are formed despite that the overall crystallinity is depleted, that is, the melting progresses in successive steps of increasing crystallite elimination and decreasing crystallite recombination until the total crystallite destruction is affected and a transparent non birefringent viscous liquid is formed. This is observed during accurate and precise melting point measurements (e.g. dilatometry or X-ray) where the polymer is given ample time in order to re-establish equilibrium while the temperature is raised very slowly, particularly near the anticipated melting point. Nevertheless, such accurate measurements are sometimes unfeasible, since the polymer may thermally degrade, or chemically react with the surrounding medium, especially at high temperatures (70).

The polyester melting point in air, or more inert surrounding as nitrogen or vacuum, falls in a temperature range from 255 deg. C to 265 deg. C; with slight variations according to the measuring method. From accurate melting point measurements, it can be discerned that actual melting starts at a given temperature, e.g. 255 deg. C, and at a different higher temperature, e.g. 265 deg. C, melting is completed. However, by quenching the polyester that has been melted to 265 deg. C, higher crystallization rates are observed, by comparison to a melt that has been heated to 290 deg. C before quenching.

This indicates that even at 265 deg. C, there are still crystallization nuclei that are difficult to detect and will not be destroyed unless the polymer melt is heated above 290 deg. C. This is a result of the polymer structure heterogeneity (70).

The amorphous and crystalline regions--although these are not two precisely defined regions; moreover different transitional regions exist--exhibit different physical properties. The density of an amorphous polyester structure is estimated to be 1.331 g/cu. cm and that of a crystalline structure 1.455 g/cu. cm. On the other hand, polyester fibers manufactured conventionally exhibit a density of about 1.39 g/cu. cm, from which it is possible to deduce an approximate degree of crystallinity of 50%. Furthermore, the polyester glass transition temperature (T_g), which is a second order transition at which the polymer molecule mobility suddenly increases, is not the same for crystalline and amorphous polyester. For amorphous polyester T_g varies from 67 deg. C to 69 deg. C and crystalline polyester T_g can be observed from 79 deg. C to 80 deg. C; depending on the method of measurement adopted. This might explain the reason for why the polyester fiber melting point, which is a first order transition, lays in a temperature range such as from 255 deg. C to 265 deg. C (70). The hot plate method for measuring the melting point is not an accurate system that is capable of discerning the polymer melting discrepancies.

Polyester Fiber Melting Point in HT-Steam

From previous observations during steaming at the higher temperatures,

the polyester fibers do not start melting at 220 deg. C, which leads to the yarn rupture, since similar yarn rupture, or flowing, is observed at steaming temperatures such as 210 deg. C and 205 deg. C--although less frequently. As the steaming temperature increases, the heat transfer rate is higher and the yarn surface reaches the ultimate temperature in shorter time periods; thereby, allowing ample time for the heat energy to raise the individual fibers temperature throughout the yarn cross section and resulting in more frequent yarn rupture; corresponding to the polyester yarn structural irregularities. However, the fibers melting process is strongly steaming temperature dependent and less time dependent; under the prevailing steaming operating conditions.

Consequently, this leads to the suggestion that during steaming the crystallite destruction in polyester may initiate at 205 deg. C, which influences extremely weak points in the yarn, and more complete melting is achieved at temperatures as high as 220 deg. C. Accurate polyester melting point measurement during steaming is restricted by the polyester susceptibility to hydrolysis, since the equilibrium establishment progression is very slow and cannot be achieved in a few minutes, but requires a few hours, which will cause severe damage to the polyester, especially under the high steaming temperature conditions.

On the other hand, the observed fiber melting on the ruptured polyester yarn ends, e.g. Figures 21 and 22 in Appendix D, might not be complete, but as it has been pointed out before: molten polyester at 265 deg. C still con-

tains crystallization nuclei that do not disappear unless the polymer is heated above 290 deg. C. This does not necessarily assume that the polyester melting point is above 290 deg. C, or the melting temperature range is from 255 deg. C to above 290 deg. C. The polymer melting is exhibited by sudden changes in its physical properties and transformation, or transition, to a viscous liquid phase. Further decrease in the molten polymer viscosity and the destruction of more small nuclei, which detection depends on the present development in instrumentation, cannot be relied upon to determine an absolute, accurate, and reproducible melting point for polymers.

The extent of polyester fibers melting that occurs during the HT-steaming at about 220 deg. C is manifested as follows: the superficial fiber melting of the broken yarn ends in Figures 21 and 22 in Appendix D, the yarn melting and necking as demonstrated in Figures 23 and 24 in Appendix D, and the yarn-linked-to-the-wire-ring experiment, which suggests a viscous liquid formation prior to the yarn flowing under its own weight. Hence, it is evident that the polyester melting point drops when subject to the superheated steam surrounding and a lower melting temperature range is exhibited, which is located between 205 deg. C and 220 deg. C; under the heat and mass transfer conditions prevailing in the steamer.

Steam Mass Flow Rate Effect on Polyester

Increasing the heat transfer rate from the flowing superheated steam to the polyester fibers necessarily increases the water molecules mass transfer into

the polyester structure; thereby, facilitating the molecular chain vibrations (both in amplitude and frequency), breaking the hydrogen bonds, and restoring more water molecules into the structure, which promotes the polymer chain flowing, mobility, and disentanglement, and ultimately results in the polyester yarn rupture.

Therefore, the steam mass flow rate strongly influences the polyester fibers melting characteristics that are only observed when the steam mass flow rate is around 16 Kg/hr (35.3 lb/hr) or more, however, if the flow rate is decreased to less than 8 Kg/hr (17.6 lb/hr) none of the polyester melting will occur as anticipated, even at temperatures as high as 230 deg. C. Under the latter conditions, most of the heat supplied to the yarn will be by radiation from the pipe wall rather than by convection from the superheated steam flow. This indicates that higher polyester chain mobility is achieved at lower steaming temperatures due to the increasing water molecules concentration in the polyester structure at high steam mass flow rates.

Generally speaking, when the heat is transported to the yarn by convection from the steam flow, the overall heat transfer coefficient is much higher than that of radiation under similar temperature gradient conditions (39); therefore, by decreasing the steam flow rate, more time will be necessary to raise the yarn temperature. Consequently, increasing the steam flow rate increases the heat transport rate to the yarn, results in higher polymer chain mobility at lower temperatures, improves the dye penetration, and decreases

the residence time necessary for satisfactory dyeings to be effected.

The water molecules diffusion rate in polyester is proportional to the temperature and the steam velocity around the fibers. For a given temperature, the water molecule diffusion rate is proportional to the steam velocity, however, as the steam velocity decreases and the temperature is to remain unchanged, not only do the water diffusion rate decrease, but because more thermal energy must be supplied by radiation, the concentration values of the water molecules in equilibrium with the polymer also decrease. (The steam radiation is negligible by comparison to the convective heat transport by the steam, or radiation from the pipe wall.)

During heat convection, the water molecule in the gas phase approaches the polymer and releases its heat energy, as kinetic energy, to the stationary water molecules on the polymer surface, which by conduction transport the heat to the polymer interior, whereas the gas molecule is instantaneously compensated with more energy from the neighboring gas molecules and driven away from the polymer surface vicinity due to the nature of the turbulent flow. However, any depletion in the stagnant water molecules layer on the polymer surface, due to diffusion into the polymer, is readily counterbalanced from the surrounding gas molecules; depending on the steam velocity. By decreasing the steam heat convection duty, less water molecules approach the polymer and more heat is transported to the yarn by radiation; thereby, decreasing the mass flow rate and varying the equilibrium conditions such that the

polyester water content decreases, since a decrease in the steam mass flow rate and velocity is necessarily accompanied by a decrease in the flow pressure. This might elucidate the polyester melting point characteristics variation at low steam flow rates.

Steaming at 200 deg. C is the highest convenient steaming temperature that can be safely controlled under the operating conditions, and results in consistent and reproducible yarn dyeing.

Higher Temperature Steaming Effects on the Polyester Yarn Tenacity

It was possible to collect a polyester yarn, 4.6 m (15 ft) long, that had been continuously dyed; by padding with the disperse dye solution, then steaming for a residence time of 2 min at about 220 deg. C. After a thorough rinsing with cold water then scouring (as described in Chapter III) in order to remove the unfixed disperse dye, the sample was left to dry at room temperature.

An Instron tester was used to determine the yarn breaking load under a constant extension rate of 12.7 cm/min (5 in./min) and a 25.4 cm (10 in.) gauge length. The average breaking load was found to be 410 g, however, some samples exhibited breaking loads of 360 g or less. By comparison to the untreated yarn breaking load of 770 g, an average decrease of 47% in the yarn tensile strength is observed. Furthermore, the average undyed polyester yarn breaking extension dropped from 26% to 15% for the continuously dyed yarn, which amounts to a 42% decrease in the breaking length.

From the load-elongation curves of both the untreated and steamed polyester yarn in Figures 28 and 29 respectively, in Appendix D, it is possible to notice that the steamed yarn exhibits a brittle rupture and does not show the S-shaped characteristics of the untreated polyester yarn. The dyed polyester yarn brittleness might be attributed to the polymer hydrolysis and--although, to a lesser extent--an increase in the crystallinity fraction. On the other hand, the decrease in the yarn tensile strength might also be due to the polyester hydrolysis as well as the polymer disorientation.

By comparing the undyed polyester fibers in Figure 16 in Appendix D and the steamed polyester fibers in Figures 18, 19, and 20 in the same Appendix, an increase in the average fiber diameter is readily noticed. The resulting shrinkage reduces the degree of the fiber orientation, which might have a certain contribution to the decrease in the steamed polyester yarn tenacity. Despite that the shrinkage (expressed as function of swelling, or increase in the fiber diameter) is about 20%, it is unlikely that such a shrinkage will cause a 47% decrease in the yarn tensile strength. An increase in the breaking extension and slight decrease in the yarn tenacity would normally be the expected results of such a shrinkage (70). But the steamed polyester yarn exhibits a 42% decrease in its breaking extension and a brittle load-elongation curve, which cannot be due solely to the fibers shrinkage. This leads to the suggestion that the decrease in the polyester yarn tenacity is chiefly attributed to the polyester hydrolysis rather than the polymer disorientation or shrinkage.

At high heat setting temperatures above 200 deg. C, in dry air, a disorientation of the crystallites along with increased crystallinity results in the case of relaxed and unstretched polyester filaments. At first the increase in crystallinity exerts a dominant influence while the disorientation manifests itself at higher temperatures. This causes a slight decrease in the filaments tenacity and invariable increase in the breaking extension. Whereas the heat setting of stretched polyester filaments do not result in any important change in the stress-strain curve characteristics; by comparison to an untreated sample. However, it has been found that the breaking load and extension of polyester fibers that are boiled in water, under the relaxed state, diminish more rapidly than when the fibers boiling is performed under tension. Steam as well as boiling water cause hydrolysis of the ester groups in the fiber; resulting in the polyester fiber loss in strength and elasticity. The degree of degradation is strongly dependent on the steam temperature, for instance, terephthalic acid is regenerated by pressure hydrolysis of polyester fiber wastes; by subjecting the latter for a period of 2 hours at 230 deg. C and 29 atm at a polyester to water ratio of 1:2, the resulting yield can be as high as 92% of crystalline terephthalic acid (70).

Therefore, it is not advantageous to conduct the continuous polyester dyeing operations under higher temperature conditions that cause partial polyester fibers melting, severe hydrolysis, and decrease in the fiber tenacity. Insignificant polyester hydrolysis is conceivable at steaming temperatures like

200 deg. C, but the dyeing under such conditions is still attractive as mentioned previously (in Chapter II), because of the high dyeing yield obtained. Nevertheless, severe polyester hydrolysis results in a sharp drop in the disperse dye fixation yields (70).

Residence Time Effect on Dye Fixation

General

From Figure 30 in Appendix D, it is obvious that the disperse dye fixation increases with the steaming residence time; for the range under investigation. The polyester-cotton blended yarn shows the higher increase in its slope with either the disperse dye, or the disperse-reactive dye mixtures. The disperse dye fixation in the blended yarn exceeds that of the polyester yarn at higher residence times. This is partly due to the blended yarn higher pick up, since more dye is fixed at longer fixation times and while the polyester yarn is limited to an average of 78% pick up, the blended yarn pick up is 154%, which takes a longer time before being consumed. The different pick up by the yarns is a direct consequence of padding three yarns of different composition simultaneously between two padding rollers that are subject to the same external pressure.

Disperse Dye Fixation Yield

Figure 31 in Appendix D shows the disperse dye fixation yield as function of the yarn pick up. The higher fixation values above 100% might be because of the disperse dye sublimed from the adjacent 100% cotton yarn in

the steamer, which can be absorbed by polyester fibers in either the blended yarn, or the 100% polyester yarn.

By considering the dye fixed at the residence time of 64.7 sec on the polyester yarn as 100% fixation and comparing with the disperse dye fixed on the blended yarn polyester component, assuming that the disperse dye fixation in the cotton component is similar to that of the 100% cotton yarn, it is observed from Figure 32 in Appendix D that the polyester fibers in the blended yarn achieve the highest dye fixation yields. This might be attributed to the good imbibition properties of the surrounding cotton fibers in the blend and their capacity during steaming to forestall the disperse dye vapor transport to the superheated steam; thereby, increasing the dye vapor pressure around the polyester fibers in the yarn interior, whereas the disperse dye vapor pressure around the 100% polyester yarn is relatively lower and no resistance is offered to the dye transfer into the surrounding flowing gas phase.

Extended Steaming Exposure Effect on the Fixed Disperse Dye

The disperse dye fixation into the fibers does not increase indefinitely with time. This is readily demonstrated from Figure 27 in Appendix D. By retaining a dyed polyester yarn in the steamer at 200 deg. C for about 20 min, the disperse dye is almost totally stripped of the yarn. The disperse dye absorption, or solution, in polyester is not due to any chemical bonds, but to secondary forces, e.g. hydrogen bonds, which cannot withhold the disperse dye molecule from subliming as the dye vapor decreases. Nonetheless, if the poly-

ester fibers are molten, the absorbed disperse dye sublimation out of the polymer becomes extremely difficult.

On the other hand, the cotton fibers are readily stripped of the disperse dye by sublimation into the flowing steam, which is due to the disperse dye low affinity for cellulose. In addition, most of the disperse dye absorbed by cellulose is mechanically occluded in the cotton fiber structure. After the yarn drying stage in the steamer, heating of the yarn initiates and the disperse dye sublimizes from the cotton fiber to the polyester, however, some of the dye vapor penetrates the cotton fiber surface and diffuses into the cellulose, or is entrapped in the fiber cavities or pores. Most of this dye can be removed afterwards during the washing process, but some dye remain enclosed in the fiber structure, even with successive wet treatments.

pH Effect on the Disperse Dye Fixation

The disperse-reactive dye mixture padding liquor is subject to different pH conditions, namely, 6 pH and 10 pH. Figure 30 in Appendix D shows the pH effect on the disperse dye fixation for the three yarns.

Varying the pH value does not appear to manifest any important influence on the polyester yarn disperse dye fixation, which reflects the polyester chemical inactivity towards the disperse dye under the HT-steaming conditions. However, acidifying the dyes liquor solution increases the disperse dye fixation on the polyester-cotton blended yarn. This cannot be due to an increase in the cellulosic component affinity for the disperse dye, since the 100% cotton yarn

exhibits a sharp decrease in the disperse dye fixation under acidic conditions. Since neither the polyester, nor the cotton component could be held responsible for the blended yarn disperse dye fixation increase under acidic conditions, hence, the dye fixation increase might be attributed predominantly to the disperse dye itself.

As mentioned previously in Chapter II, the disperse dye is usually affected under alkaline conditions and can be reduced when subject to higher alkaline pH values, especially during high temperature thermofixation. Maximum disperse dye fixation yields on polyester are attained under weakly acid conditions, which explains the dye fixation improvement manifested by the blended yarn. Nonetheless, the decrease in the disperse dye fixation in the blended yarn might be also due to the disperse dye interaction with the reactive dye, which is enhanced under alkaline conditions.

This leads to suggesting that the reason for which the 100% polyester yarn does not exhibit the expected disperse dye improvement under acidic conditions, like the blended yarn, might be attributed to the relatively low pick up of the polyester yarn, as well as the absence of the cotton fibers around the polyester, which presence provides a higher disperse dye vapor pressure and accordingly increases the disperse dye solution in polyester; thereby, resulting in higher fixation yields that are sensible to the disperse dye chemical interactions.

It is important to mention that the disperse dye padding liquor is at

about 10 pH, which increases slightly during the thermofixation. Nonetheless, this does not cause any significant polyester hydrolysis under the operating conditions, since the polyester yarn dyed under alkaline conditions (with the disperse-reactive dye mixture) does not manifest any important decrease in its disperse dye fixation by comparison to the dyeing performed under acidic conditions--the polyester hydrolysis is accompanied by a decrease in the disperse dye fixation (70).

Under the alkaline conditions, cellulose is ionized and might manifest a higher affinity for the disperse dye, whereas under acidic conditions the cellulose ionization is minimized, which would explain the decrease in the disperse dye fixation on the cotton yarn when the disperse-reactive dye padding liquor is slightly acidic (6 pH). On the other hand, under acid conditions and at high temperatures, the cellulose hydrolyses to glucose while under milder acidities hydrocellulose is formed; under both circumstances tendering results (103) and an increase in the cotton fiber structure accessibility during the washing process is possible; thereby, facilitating the disperse dye removal from cellulose and decreasing the mechanical dye occlusion. This may be partly responsible for the relative easiness with which the unfixed disperse dye is removed from the cotton fibers when the dyeing has been performed with an acid padding liquor--this is beside the fact that less disperse dye stains the cotton under acid pH values due to the decrease in the cellulose affinity towards the dye molecule.

The Reactive Dye Interference with the Disperse Dye

From Figure 30 in Appendix D, it is clear that the reactive dye presence affects the disperse dye fixation on the three yarns. The blended yarn appears to be the most influenced by the reactive dye interaction with the disperse dye. Furthermore, the pH values investigated do not manifest a strong influence on the dyes interactions, especially in the case of the polyester yarn. Hence, suggesting that the disperse dye and reactive dye possess a relatively high chemical potential for interacting under the HT-steaming conditions.

The disperse dye, 1,5-diamino-4,8-dihydroxy-monochloro-anthraquinone, and the reactive dye system, 2,4-difluoro-5-chloro-pyrimidine (FCP) are expected to interact during thermofixation, since the hydroxy and amino groups present in the disperse dye are in positions (alpha-positions) that make them active and susceptible to undergo different reactions with the highly reactive trihalogeno diazinyI group of the reactive dye (see Chapter II for further details and references).

Most of the reactive dye fixation on cellulose with the corresponding alkali consumption is accomplished during the early stages of thermofixation and before that the disperse dye starts vaporizing and diffusing into polyester. This, to a certain extent, minimizes the dye interaction, since aggregated disperse dye molecules surrounded by the dispersing agents are less susceptible to react. Nevertheless, not all the reactive dye is capable of reacting with cellulose, especially in the blended yarn with its 154% pick up. Hence, a rela-

tively large amount of unfixed reactive dye and alkali will be able to react with the disperse dye vapor, particularly in the cotton fiber regions; where the disperse dye vapor pressure and the unfixed reactive dye concentration are at their maximum--as a result of the cellulose fibers good imbibition properties. This may elucidate the sharp decrease in the disperse dye fixation due to the reactive dye presence in the polyester-cotton blended yarn; by comparison to the slighter dye interaction effect on the polyester yarn (78% pick up). Figure 31 in Appendix D clearly demonstrates the dyes interference discrepancies.

On the other hand, the decrease in the disperse dye vapor pressure due to the reactive dye vapor presence might also--although to a lesser extent--contribute to the disperse dye fixation diminution. In addition, the reduction in the disperse dye vapor pressure might induce a solid-solid transition to that of a more stable polymorph (see Chapter II).

Dyes Entrainment

The detection of dyeing ingredients entrapped in the experimenter's nostril openings during the yarn HT-steaming, led the way to further investigation on the evolving steam composition.

In an attempt to estimate the mass flow rate of dyes entrained along with the superheated steam to the surrounding atmosphere, condensed steam samples were obtained from both sides of the steamer; under the steaming temperature of 200 deg. C and residence time of 64.7 sec, and during the disperse-reactive dyes fixation under alkaline conditions (10 pH). This had been done

by placing a long glass test tube filled with ice such that the bottom of the tube is at about 10 cm above the steamer outlet; the condensed droplets were successively collected in a 20 cu. cm capacity test tube fitted with a cork stopper in order to prevent further condensate evaporation.

It was found from spectrophotometric analysis that the steam condensate composition is the same from both sides of the steamer. From the Beer's law for multicomponent solutions, the condensate composition was estimated; 0.00416 g/l. disperse dye and 0.0031 g/l. reactive dye (use was made of the absorption data from Chapter III). Since the rate of steam evolution is about 16 Kg/hr, hence, 0.0666 g/hr disperse dye and 0.0496 g/hr reactive dye are transported to the surrounding atmosphere.

Furthermore, it is possible to estimate the percentage of dye lost to the atmosphere with respect to that padded on the yarns. It can be readily shown that the mass flow rate of a yarn that is fed to the steamer for a 64.7 sec residence time, is about 2.43 g/hr (see Chapter III). From the padding liquor for each yarn (polyester yarn, 78%; blended yarn, 154%; and cotton yarn, 106%) and the yarn mass flow rate (2.43 g/hr), the padding liquor flow rate to the steamer is 8.2 g/hr. Since the padding liquor density is around 1.15 g/cu. cm and both the disperse dye and reactive dye are at the same concentration, i.e., 50 g/l., hence, the mass flow rate of either dyes fed to the steamer is 0.357 g/hr. Thus by comparison to the dye flow rate evolved with the steam, about 2.37% of the disperse dye and 1.77% of the reactive dye are gone with the steam.

Figure 33 in Appendix D shows the light absorption spectra of the actual condensed steam solution and a dye solution made up according to the estimated disperse dye and reactive dye concentrations. Both solutions exhibit the same maximum absorption wave length (600 nm); although, the simulated solution spectrum cannot be superimposed on the condensate solution spectrum, particularly in the short wave length range (yellow region). This can be attributed to a relatively high dispersing agent content in the evolved steam--the dispersing agent possesses a yellowish green color in water solutions (see Chapter III).

Hence, the steam evolved contains disperse dye, reactive dye, and a considerable amount of dispersing agent. However, by comparing the two solution spectra in Figure 33 in Appendix D, it can be deduced that the estimated dye concentrations are actually slightly lower than in the steam condensate solution; although the estimated values are already alarming. Nevertheless, the dye vapors can be minimized by padding less dyes on the yarns, e.g. 70% pick up is commonly used in industry for the polyester-cotton blend.

Fiber Swelling

The yarns HT-steaming is at the same time a heat-setting process and the polyester fiber shrinkage would be expected to occur, since the individual fibers in the yarn are practically under no tension (see Chapter II). Steaming at 220 deg. C resulted in an average swelling of 20% after a residence time of 21.6 sec; as mentioned previously in this Chapter. Less shrinkage, or swelling,

would be anticipated at lower temperatures like 200 deg. C . Extended steaming times enhance the polyester fiber swelling, however, swelling is more temperature dependent (70).

On the other hand, the superheated steam effect on the cotton fiber swelling had been investigated, but no important dimensional variations in the cellulosic fiber were observed; as shown from Figures 25 and 26 in Appendix D.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

HT-steaming thermofixation is achieved--without intermediate drying--for continuously dyeing polyester-cotton blended yarns with disperse-reactive dye mixtures. Drying, dyeing, and heat-setting can all be performed efficiently during the HT-steaming. Simple padding liquor formulation can produce high dye fixation yields at 200 deg. C and for a residence time of about 1 min--provided that the disperse dye and reactive dye do not interact. In addition, the cotton fiber presence in the blend improves the disperse dye fixation on the polyester component.

The polyester fiber melting point drops under the HT-steaming conditions due to the water molecule penetration into the polymer structure, which is function of the steaming mass flow rate around the fibers. Furthermore, higher steaming temperatures and longer residence times might induce polyester hydrolysis, disorientation, and losses in the fiber tenacity.

High padding liquor pick up can cause pollution problems due to the entrainment of disperse and reactive dye vapors with the evolved steam into the surrounding atmosphere.

Recommendations

It is possible to simulate the variations that take place as the yarn steaming progresses throughout the steamer pipe length. This can be done by steaming different yarn samples for varying residence times. The yarn sample could be mounted on a wire frame and rapidly introduced in the steamer for a predetermined time period, then, immediately pulled out and examined. Variations such as yarn padding liquor composition, dye fixation, fiber orientation and crystallization, hydrolysis, tenacity, and partial melting can be plotted versus the steamer length; therefrom, modifications in the steamer design or operating conditions might be advantageous. In addition, the influence of residence time, steaming temperature, dye liquor concentration, pick up, and steam mass flow rate on the fibers physical and chemical structure can be explored at different ranges. However, other heating media can also be investigated, e.g. dry air or vapor mixtures, and the results compared with those obtained from using steam.

Another interesting study would be to examine the polyester melting point variation at higher steaming mass flow rates and particularly in water, when heated under pressure; above 100 deg. C. Similarly, the influence of other vapors on the polyester melting can be further explored.

Furthermore, the dye evolution with the steam to the surrounding atmosphere needs to be studied as function of the padding dye liquor composition, material pick up, steaming temperature, residence time, and steam mass flow

rate.

The reactive dye fixation on the cotton component of the blend may be explored, e.g. by using the skeleton method (see Chapter II). Different dye fixation evaluation methods by light reflectance and absorption can be used to investigate the dyes penetration in the material.

It would be advantageous to use a padder equipped with a steel roller and a heavy duty rubber roller; instead of the polypropylene coated rollers, which might be damaged when used for padding yarns continuously. In addition, a variable speed motor for driving the padding rollers would offer more possibilities for the residence time variation and control. Moreover, a take-up system capable of collecting the yarns without manual interference will facilitate the yarns processing.

The use of a glass thermometer to measure the temperature throughout the steamer is tedious. Three thermocouples with stainless steel sheath can be introduced through different sections of the steaming pipe and the temperature recorded as function of time. The variable transformers would be manually adjusted such that the thermocouples give similar temperature readings. Thereby, it might be possible to examine--in one run only--the dye fixation, or other variations, as function of a wide temperature range for a specific residence time; by knowing the speed at which the yarns are collected on the take-up bobbins, since each yarn section steaming temperature can be traced back with the aid of the temperature recorder chart.

Economic studies can be made on the HT-steaming process in order to determine the operating costs per unit mass of material at different dye fixation yields and under varying steaming conditions; therefrom, optimum operating conditions are estimated and modifications in the steamer design might be necessary for commercial production.

APPENDIX A
INTRODUCTION

APPENDIX A

Table 1. Historical Development of Synthetic Dyes

| Year | Discoverer | Dye | Dye Class | Reference |
|------|-------------------------|------------------------------------|-----------------------|-------------|
| 1771 | Woulfe | picric acid | acid | (93) |
| 1834 | Runge | resolic acid | acid | (76) |
| 1856 | Perkin | Mauveine | basic | (93), (76) |
| 1858 | Verguin | fuchsine | basic | (103) |
| 1858 | Griess | diazotization reaction | azo dyes | (93), (103) |
| 1863 | Martius | Bismark Brown | acid (azo) | (93) |
| 1868 | Graebe and Lieberman | Alizarin | mordant | (93) |
| 1870 | van Baeyer | indigo | vat | (93), (1) |
| 1880 | Huddersfield | Para Red | azoic, solvent | (1), (108) |
| 1884 | Bottiger | Congo Red | direct | (103), (1) |
| 1890 | Bayer Co. | Diamond Blue F after-chrome dye | mordant | (103) |
| 1893 | Vidal | Sulphur Black | sulphur | (93), (103) |
| 1900 | Berlin Aniline Co. | meta-chrome dyes | mordant | (103) |
| 1901 | Bohn | Indanthrene Blue | vat (anthraquinonoid) | (93), (103) |

Table 1. Historical Development of Synthetic Dyes (Continued)

| Year | Discoverer | Dye | Dye Class | Reference |
|------|-----------------------|--|--|--------------------|
| 1919 | CIBA | Neolon 1:1 metal azo complex dyes | metal complex acid dyeing pre- metallized | (1), (103) |
| 1920 | Ellis | S.R.A. colors | disperse | (1), (76) (103) |
| 1921 | Bader and Sunder | Indigosol O | leuco vat | (1) |
| 1950 | Goodall | Irgalan 1:2 metal azo complex dyes | metal complex neutral-dyeing pre- metallized | (76), (103) |
| 1952 | CIBA | Cibalan | reactive (for wool) | (1), (93) |
| 1956 | Rattee and Stephen | Procion | reactive (for cellu- lose) | (1), (93) |

Table 2. Regenerated Man-Made Fibers

| Year | Discoverer | Fiber | Class | Reference |
|------|-----------------|-----------------------------|-------------------|-------------|
| 1869 | Schutzenburger | cellulose triacetate rayon | cellulose acetate | (76), (103) |
| 1884 | Chardonnet | nitrocellulose rayon | rayon | (53), (103) |
| 1892 | Cross and Bevon | viscose rayon | rayon | (53), (103) |
| 1897 | Pauly | cuprammonium rayon | rayon | (103) |
| 1905 | Miles | secondary cellulose acetate | cellulose acetate | (103) |
| 1935 | Ferretti | casein | protein | (76) |

Table 3. Synthetic Man-Made Fibers

| Year | Discoverer | Fiber | Class | Reference |
|------|-----------------------|--|---------------------|--------------------|
| 1932 | Carothers | nylon 6 poly(6-aminocaproic acid) | polyamide | (76) |
| 1936 | Carothers | nylon 66 poly(hexamethylene adipamide) | polyamide | (53), (76) |
| 1940 | Whinfield and Dickson | Terylene poly(ethylene terephthalate) | polyester | (53), (76) (92) |
| 1940 | Dow Chemical | Saran poly(vinylidene chloride-co-vinyl chloride) | vinylidene chloride | (76) |
| 1942 | du Pont | Orlon poly(acrylonitrile) | acrylic | (76) |

Table 3. Synthetic Man-Made Fibers (Continued)

| Year | Discoverer | Fiber | Class | Reference |
|------|---------------|---|-------------------------|------------|
| 1947 | du Pont | Spandex polyurethane | snap-back | (53), (76) |
| 1948 | Union Carbide | Vinyon N poly(vinyl chloride-co- acrylonitrile) | modacrylic | (53), (76) |
| 1950 | Toyo Koatsu | Urylon poly(urea nonamethylene) | polyurea | (76) |
| 1954 | du Pont | Teflon polytetrafluoroethylene | polytetrafluoroethylene | (76) |
| 1961 | du Pont | Nomex poly(m-phenylene isophthalamide) | polyamide aromatic | (76) |
| 1962 | Montecatini | Meraklon polypropylene | polyolefin | (53), (76) |
| 1966 | Cipriani | nylon 6-T poly(hexamethylene terephthalamide) | polyamide aromatic | (76) |
| 1968 | Nippon Rayon | A-Tell polyethyleneoxybenzoate | polyesterether | (76) |

Table 4. Fibers Dyeing (19)

| | Cotton | Wool | Silk | Rayon | Cellulose Acetate | Acrylic Modacrylic | Polyester | Polyamide | Polyolefins |
|--------------------|--------|------|------|-------|----------------------|-----------------------|-----------|-----------|-------------|
| Acid | 0 | \$ | \$ | 0 | 0 | (\$) | 0 | \$ | 0 |
| Acid Metallized | 0 | \$ | \$ | 0 | 0 | (\$) | 0 | \$ | 0 |
| Acid-NDM | 0 | \$ | \$ | 0 | 0 | (\$) | 0 | \$ | 0 |
| Mordant | 0 | \$ | \$ | 0 | 0 | (\$) | 0 | \$ | 0 |
| Basic | 0 | 0 | 0 | 0 | 0 | \$ | (\$) | (\$) | 0 |
| Vat | \$ | \$ | \$ | \$ | 0 | 0 | 0 | 0 | 0 |
| Leuco-Vat | \$ | \$ | \$ | \$ | 0 | 0 | 0 | 0 | 0 |
| Sulphur | \$ | 0 | 0 | \$ | 0 | 0 | 0 | 0 | 0 |
| Disperse | 0 | 0 | 0 | 0 | \$ | \$ | \$ | \$ | 0 |
| Direct | \$ | \$ | \$ | \$ | 0 | 0 | 0 | \$ | 0 |
| Azoic | \$ | 0 | 0 | \$ | \$* | \$* | \$* | \$* | 0 |
| Reactive | \$ | \$ | \$ | \$ | 0 | 0 | 0 | 0 | 0 |
| Solvent | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

\$ = commercially used

(\$) = commercially used on a chemically modified fiber

\$* = can be commercially used, but requires special dyeing techniques

0 = not commercially used

APPENDIX B

LITERATURE SEARCH

APPENDIX B

Table 5. Physical and Mechanical Properties of Cotton and Polyester Fibers (78).

| Property* | Cotton (Sea Island) | Polyester (Terelene) |
|--|------------------------|--|
| Density on Dry Basis (g/cu. cm) | 1.55 | 1.39 |
| Specific Heat (cal/g/deg. C) | 0.29 | 0.32 |
| Coefficient of Linear Expansion in Fiber Axis Direction (% expansion/deg. C) | - | 0.5 |
| Mass Specific Electrical Resistance (M ohm-g/sq. cm) | 6.31 | 100. |
| Refractive Indices | | |
| Axis Direction (n_{\parallel}) | 1.578 | 1.725 |
| Perpendicular Direction (n_{\perp}) | 1.532 | 1.537 |
| Birefringence ($n_{\parallel} - n_{\perp}$) | 0.046 | 0.188 |
| Crystallinity (%) | 70 | 50 |
| Official Regain Allowance (%) | 7 | 0.4 |
| Heat of Wetting from Zero Regain (cal/g) | 11. | 1.2 (2 denier) 0.56 (4 denier) 0.39 (8 denier) |
| Tenacity (g wt./tex) | 46 | 48 |

Table 5. (Continued)

| Property* | Cotton (Sea Island) | Polyester (Terelene) |
|---|------------------------|-------------------------|
| Breaking Extension (%) | 6.8 | 37 |
| Work of Rupture (g wt./tex) | 1.52 | 12.1 |
| Initial Modulus (g wt./tex) | 740 | 900 |
| Specific Torsional Rigidity (g wt.-sq. cm/sq. tex) | 7.9×10^{-4} | 4.8×10^{-4} |
| Shear Modulus (dyn/sq. cm) | 2.51×10^{10} | 0.91×10^{10} |

* All measurements were made under standard conditions of 65% relative humidity and 20 deg. C, unless specified.

Table 6. Complementary Properties of Cotton and Polyester (53).

| Property | Cotton | Polyester |
|-----------------------|--------|-----------|
| Wrinkle Recovery | - | xxx |
| Wet Press Retention | - | xxx |
| Absorbency | xxx | - |
| Static Resistance | xxx | - |
| Resistance to Pilling | xxx | - |
| Strength | xx | xxx |
| Abrasion Resistance | x | xxx |
| Stability | xx | xxx |
| Resistance to Heat | xxx | x |

xxx = Excellent

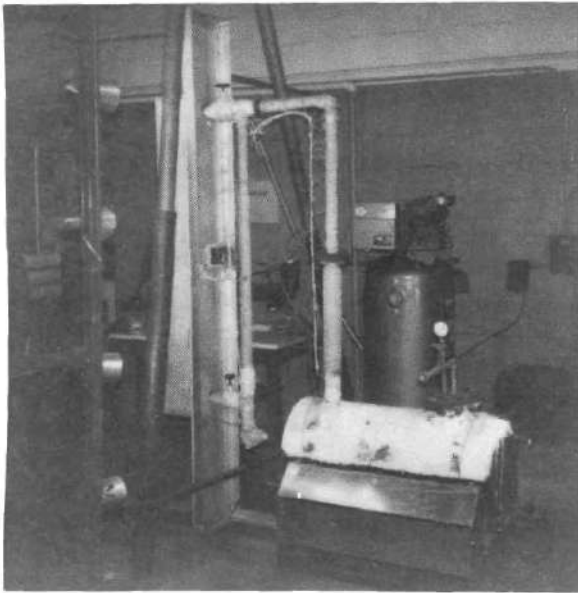
xx = Good

x = Fair

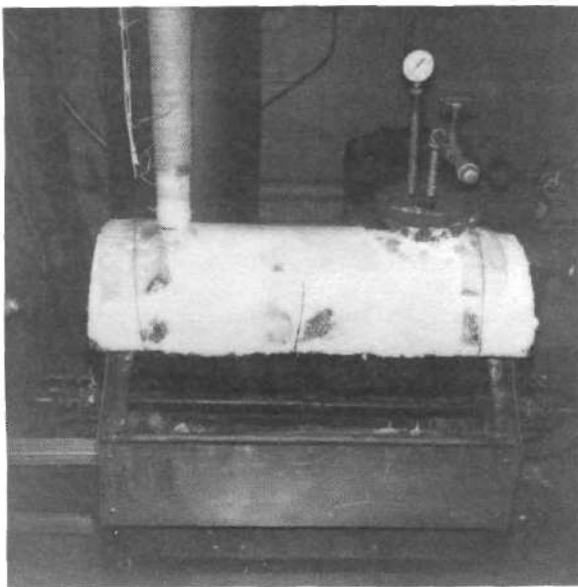
- = Deficient

APPENDIX C

EXPERIMENT DESIGN



GENERAL VIEW



BOILER VESSEL

Figure 1. Boiler

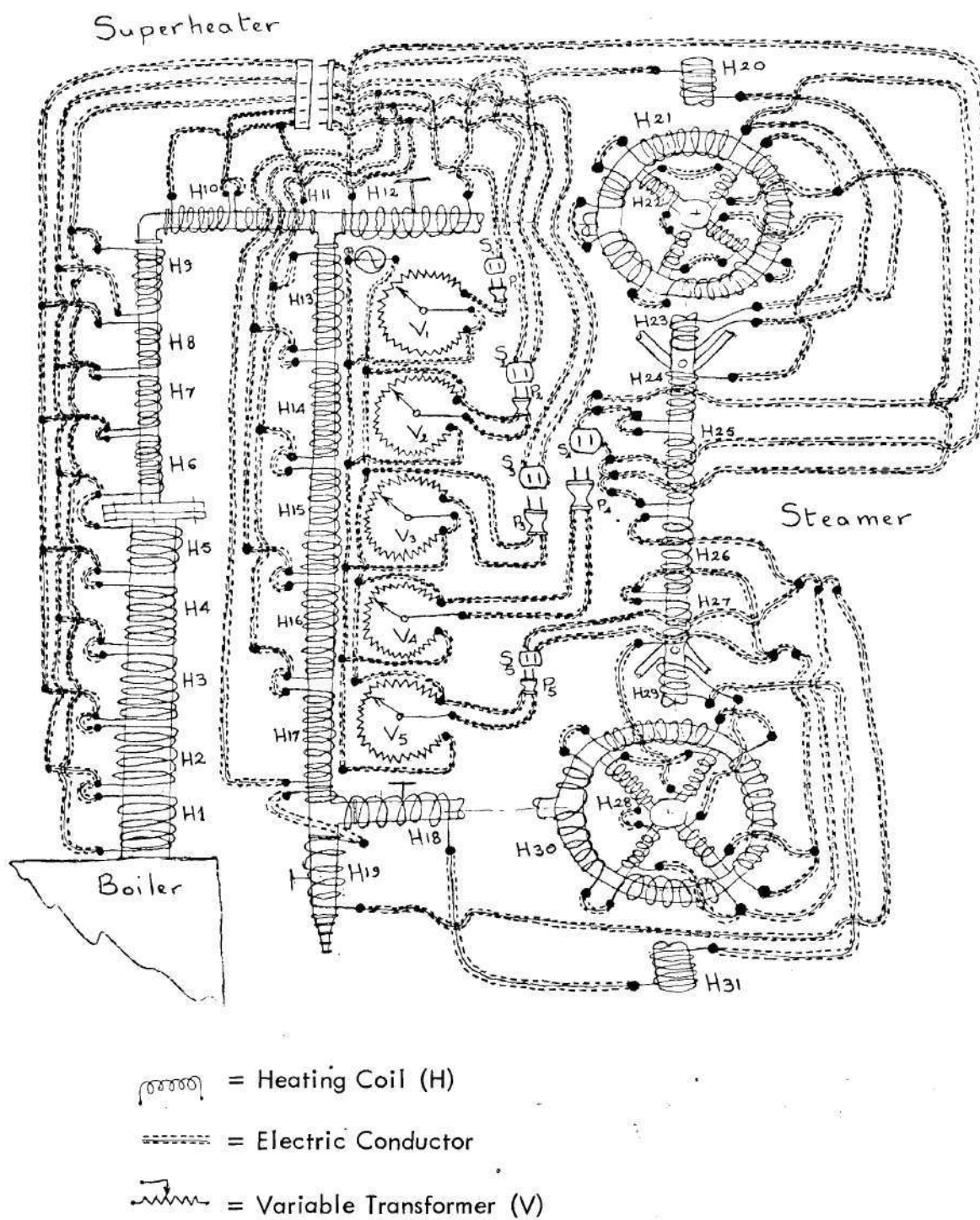
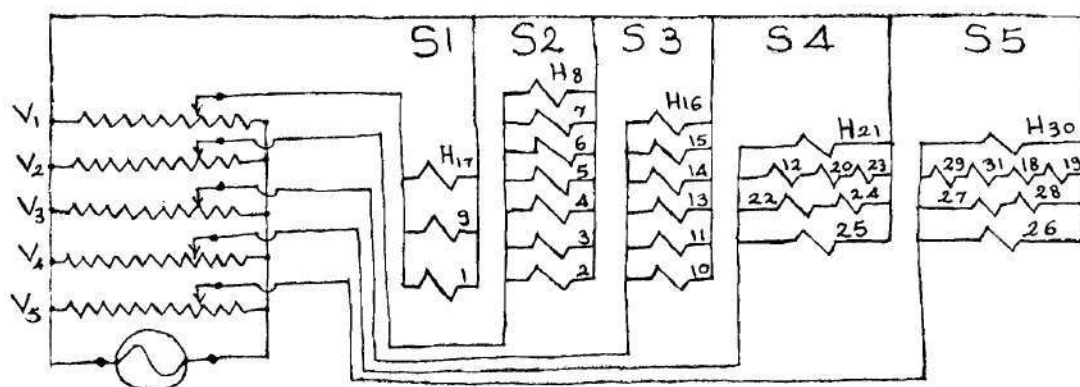
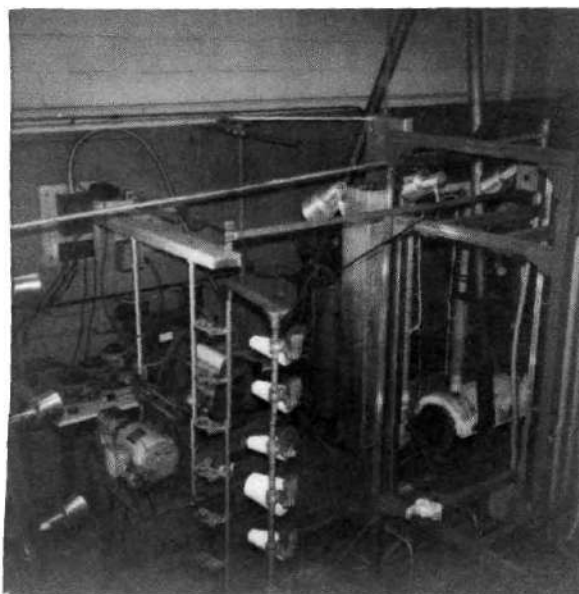


Figure 2. Sketch of the Electric Heating System

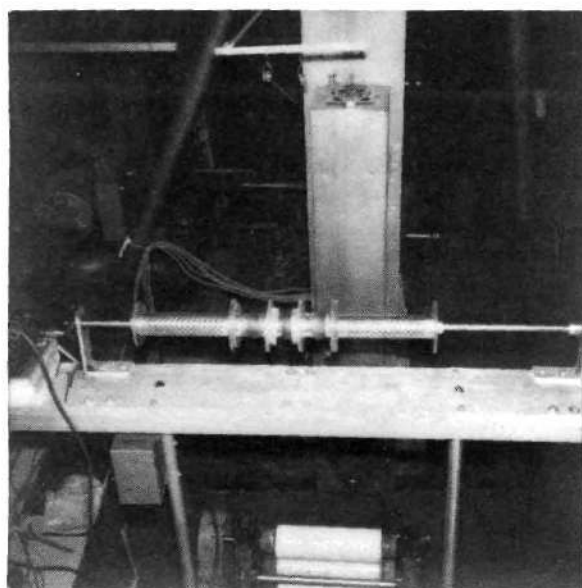


S = Heating Section
 V = Variable Transformer
 H = Heating Coil

Figure 3. Temperature Control Electrical Diagram

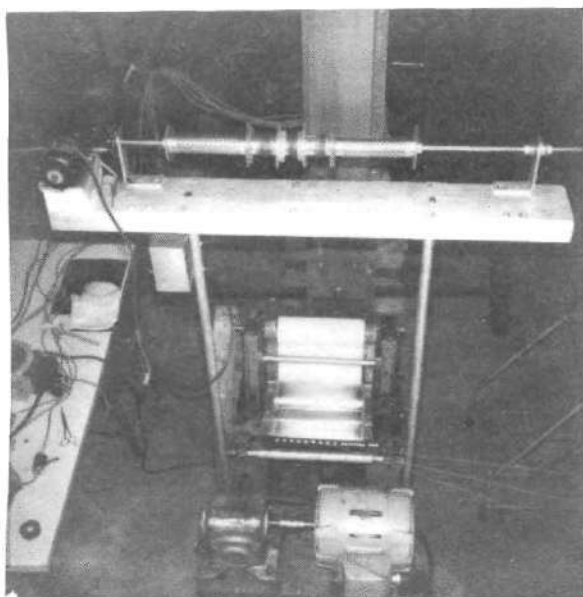


GENERAL VIEW

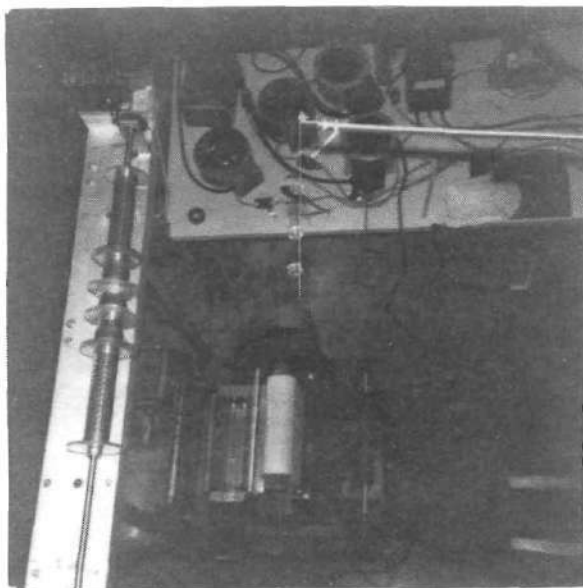


STEAMER UNIT (back)
TAKE-UP SYSTEM (front)
PADDING ROLLERS (below)

Figure 4. Steamer



GENERAL VIEW



TAKE-UP SYSTEM (left side)
PADDER (below)
DRIVING PULLEYS (middle)
VARIABLE TRANSFORMERS
(background)

Figure 5. Padder and Take-Up Systems

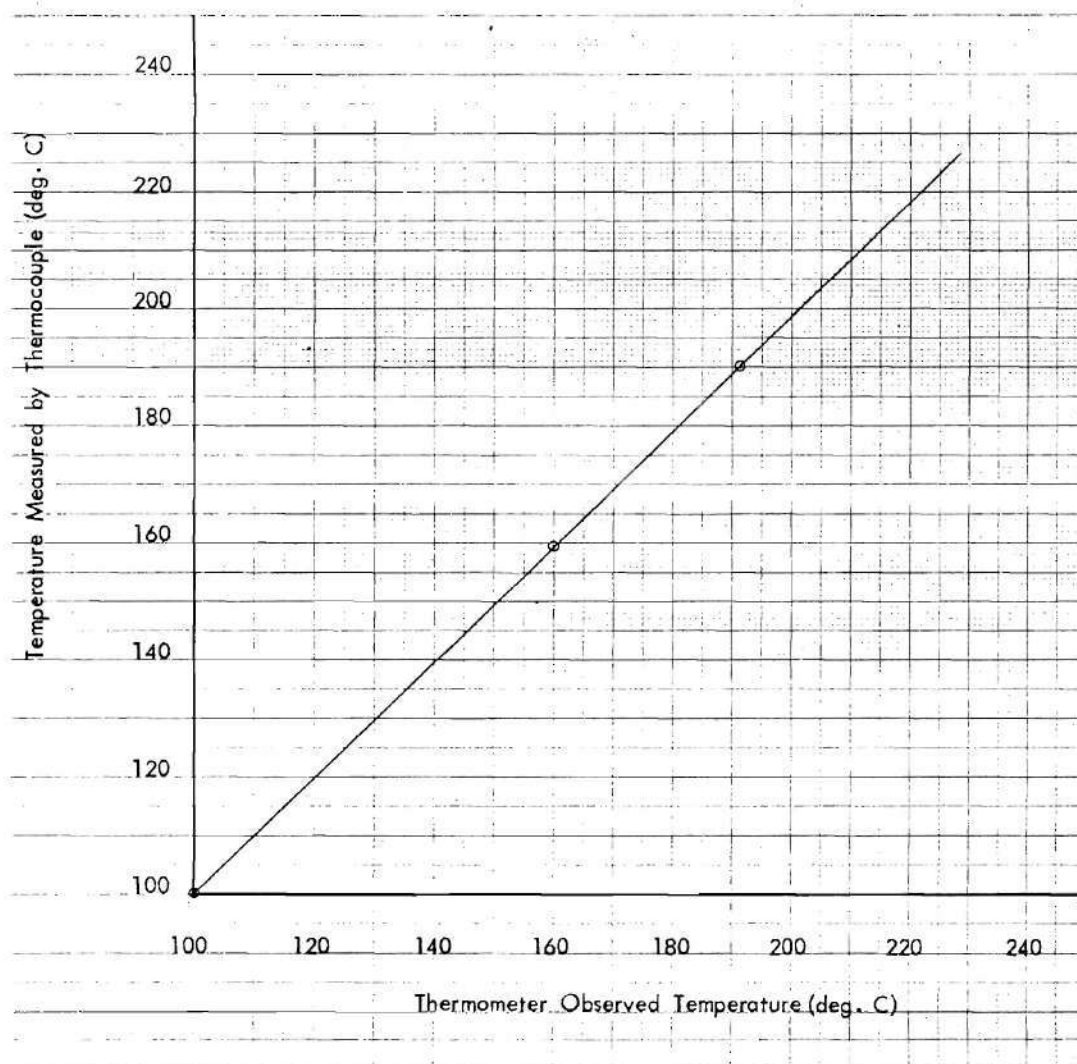
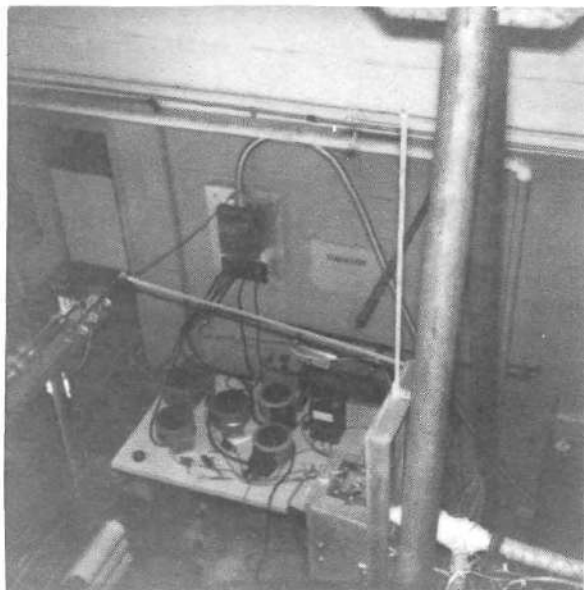
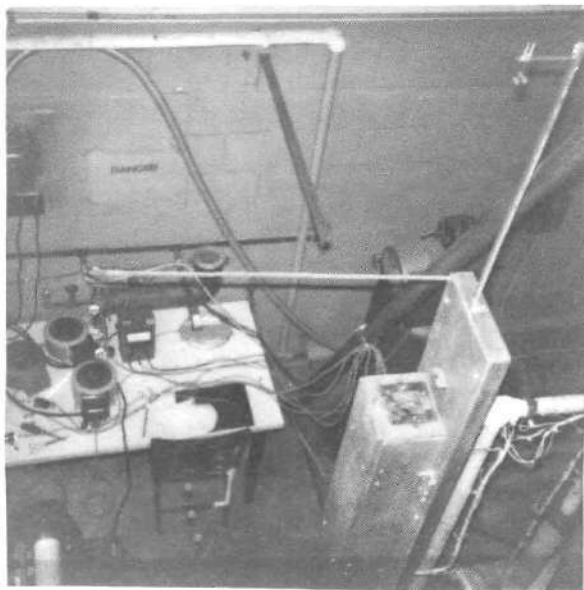


Figure 6. The Thermometer Calibration

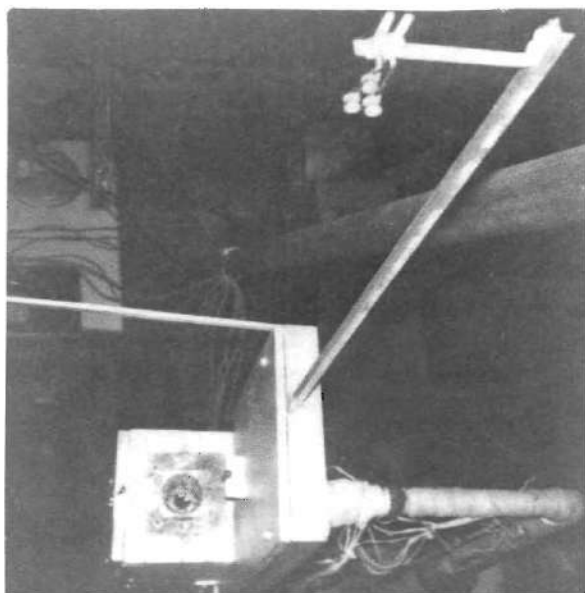


GENERAL VIEW

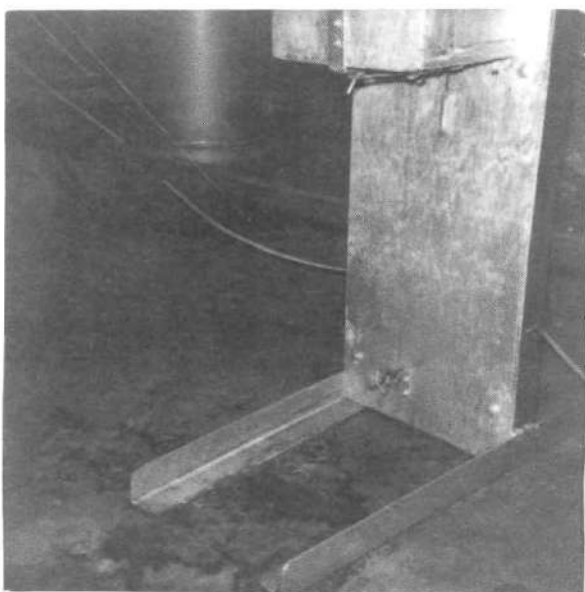


YARNS DRIVING OUT
OF THE STEAMER TO
THE TAKE-UP SYSTEM

Figure 7. Yarns Driving



GUIDING PULLEYS
ABOVE STEAMER



GUIDING PULLEYS
DRIVING YARNS FROM
PADDING ROLLERS TO
STEAMER

Figure 8. Guiding Pulleys

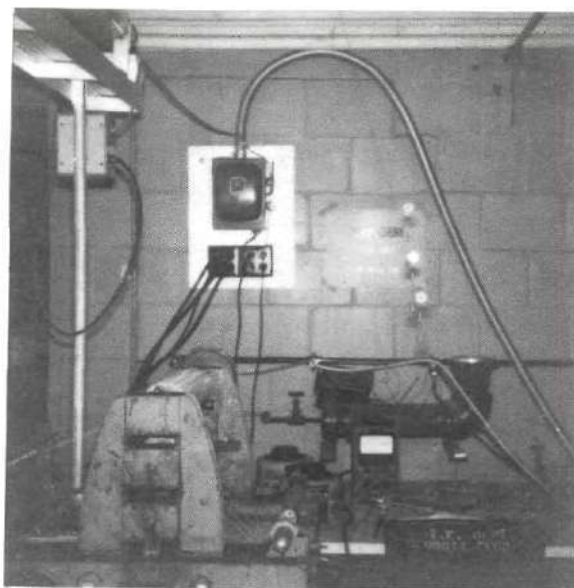


Figure 9. Pending Weight from Tensioning Pulley (middle)

G.P. = Guiding Pulley
 T.P. = Tensioning Pulley

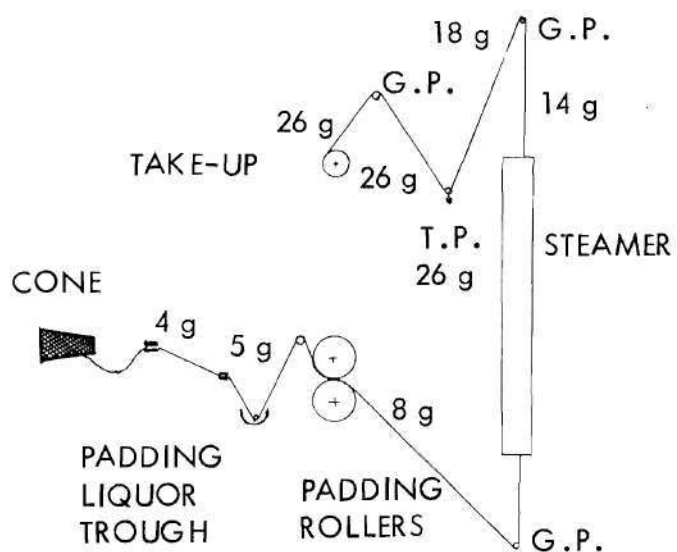


Figure 10. Tension Force (in gram weight, g) Distribution on the Driven Yarn

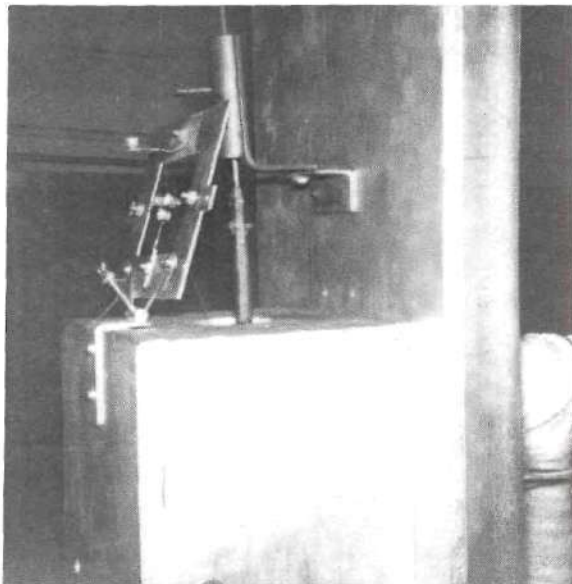
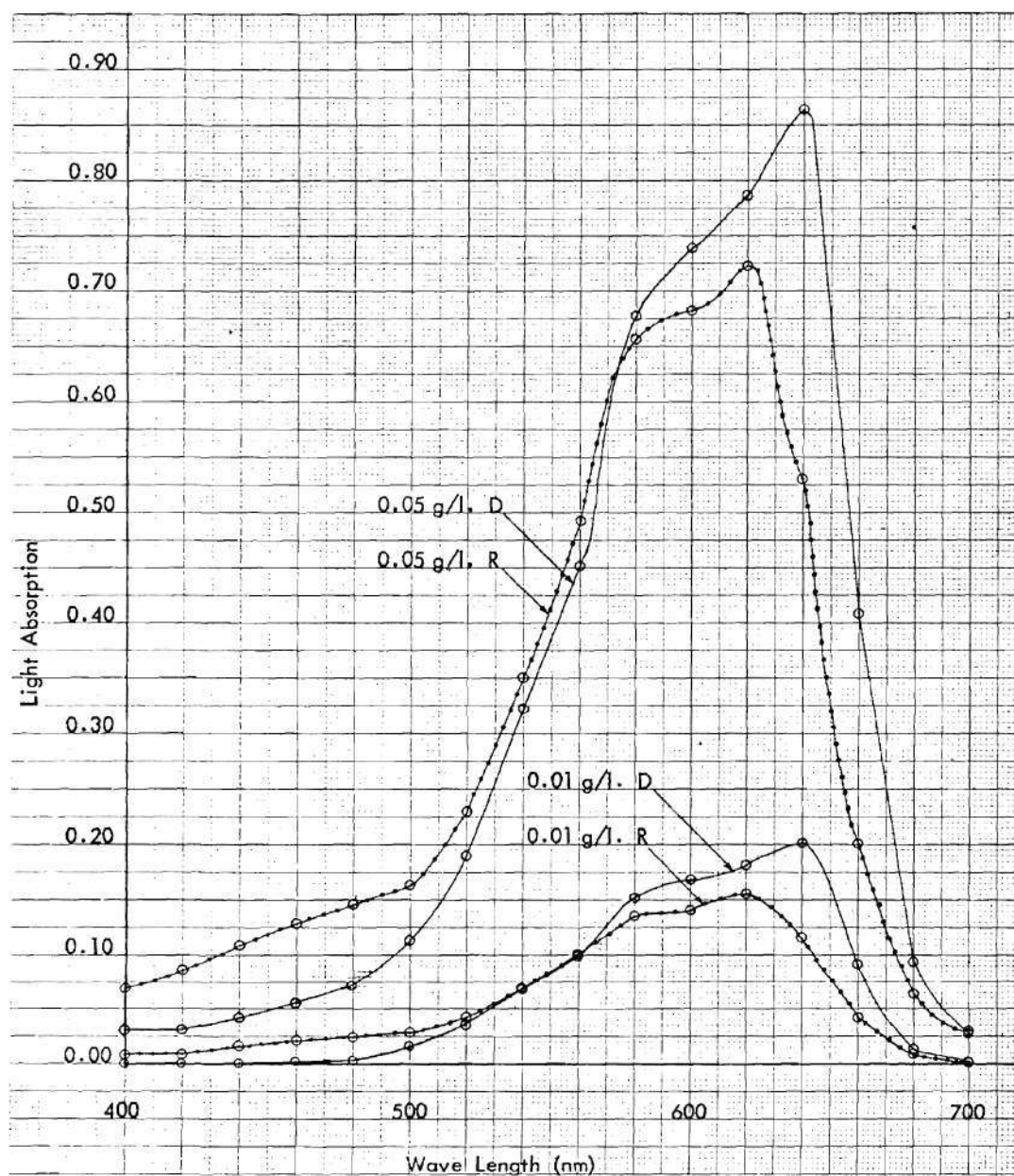
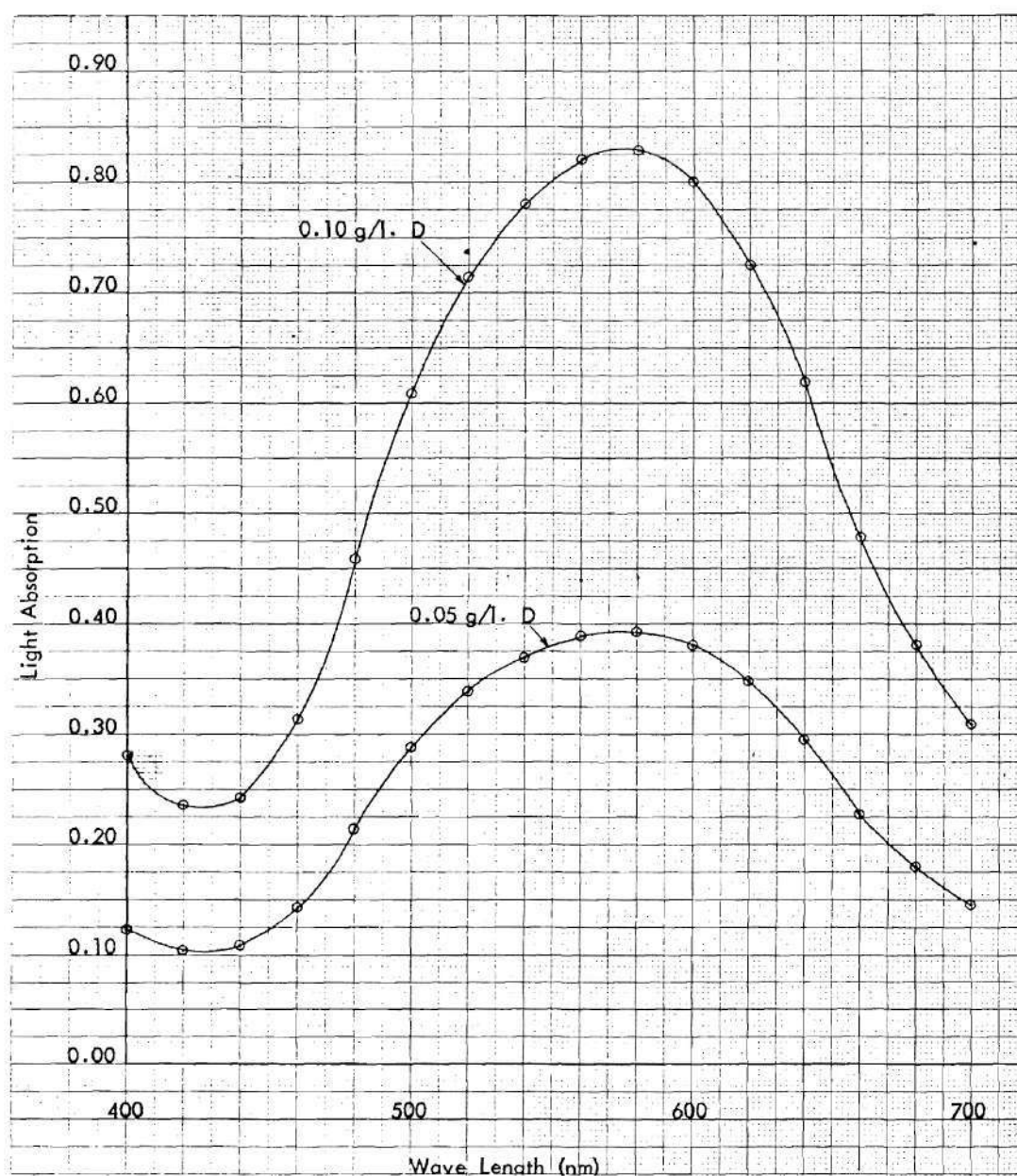


Figure 11. Yarn Holder



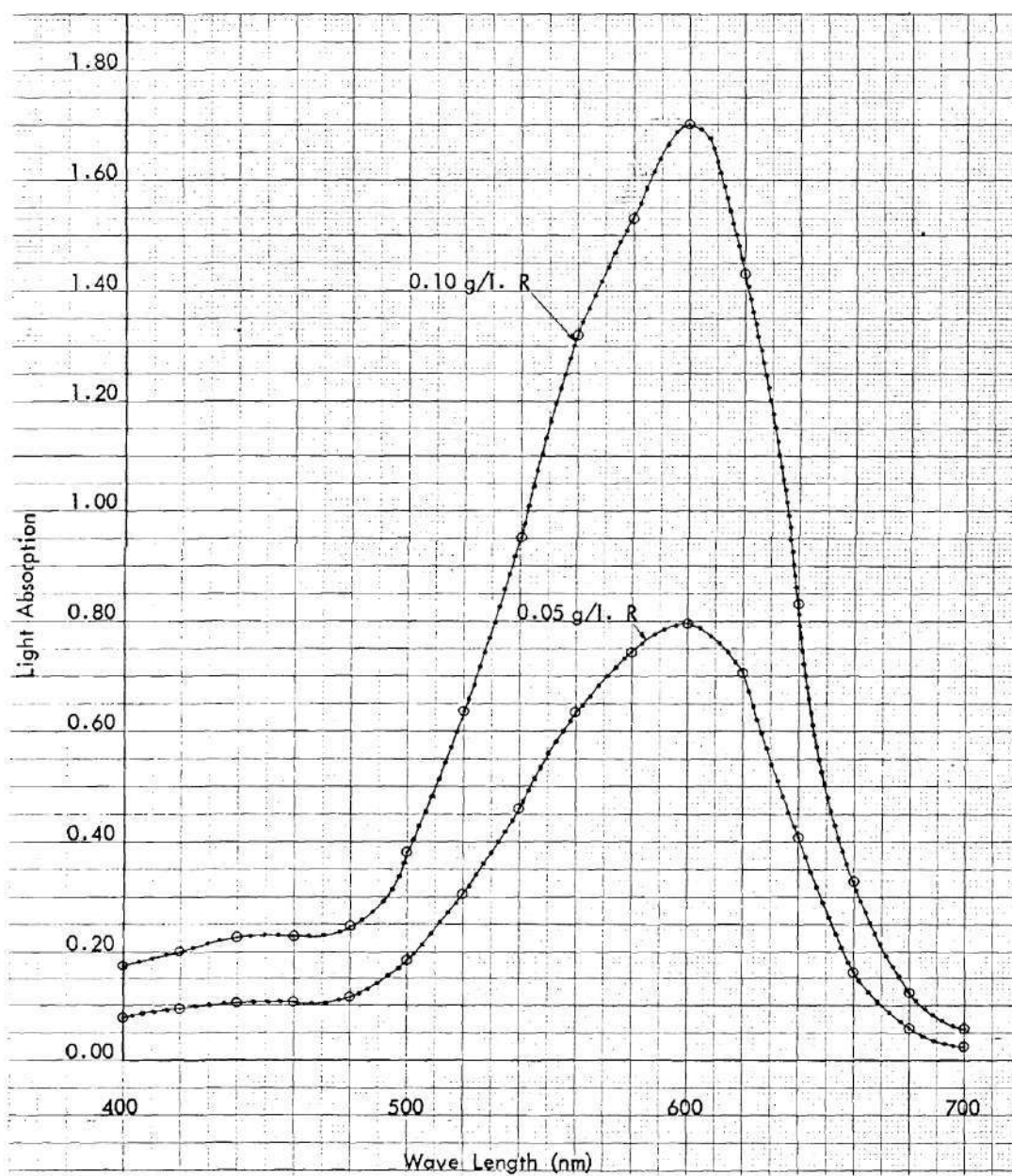
D = Disperse Dye
R = Reactive Dye

Figure 12. Spectra of Dyes Dissolved in DMF Solutions at Different Concentrations (in g/l.) [Data is from Tables 7 and 8 in Appendix C]



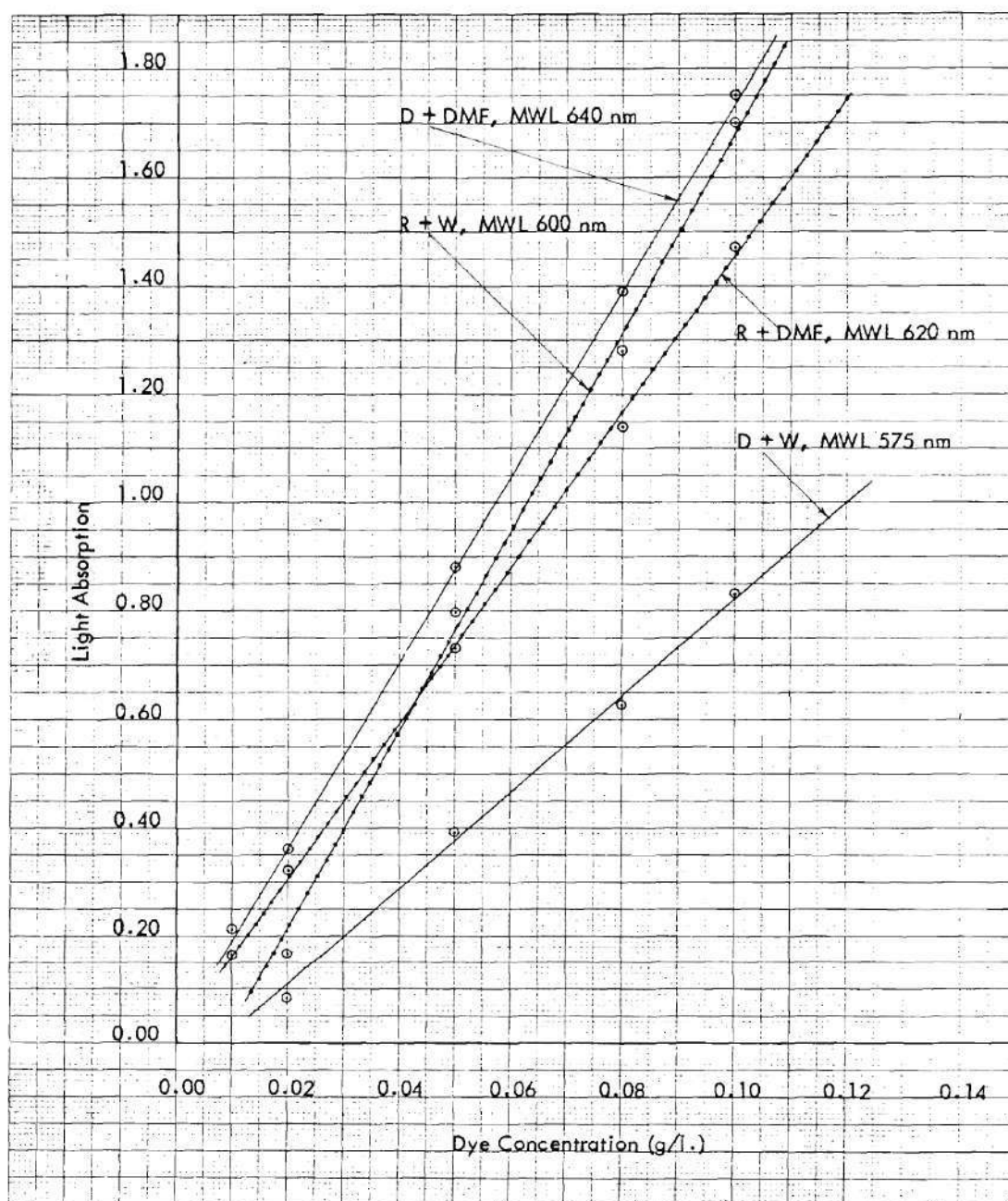
D = Disperse Dye

Figure 13. Spectra of Disperse Dye Dissolved in Water at Different Concentrations (in g/l.) [Data is from Table 7 in Appendix C]



R = Reactive Dye

Figure 14. Spectra of Reactive Dye Dissolved in Water at Different Concentrations (in g/l.) [Data is from Table 8 in Appendix C]



D + DMF = Disperse Dye Dissolved in DMF
 D + W = Disperse Dye Dissolved in Water
 R + DMF = Reactive Dye Dissolved in DMF
 R + W = Reactive Dye Dissolved in Water
 MWL = Maximum Light Absorption Wave Length (in nanometer, nm)

Figure 15. Relation between Dye Concentration and Light Absorption
[Data is from Table 9 in Appendix C]

Table 7. Light Absorption of Disperse Dye Solutions

| Wave Length in Nanometer (nm) | Light Absorption of Disperse Dye Solutions* | | | |
|-------------------------------------|---|-------|--------------------------|-------|
| | Water | | DMF | |
| | Dye Concentration (g/l.) | | Dye Concentration (g/l.) | |
| | 0.100 | 0.050 | 0.050 | 0.010 |
| 400 | 0.280 | 0.123 | 0.031 | 0.000 |
| 420 | 0.235 | 0.104 | 0.031 | 0.000 |
| 440 | 0.242 | 0.109 | 0.042 | 0.000 |
| 460 | 0.313 | 0.143 | 0.055 | 0.002 |
| 480 | 0.458 | 0.214 | 0.072 | 0.005 |
| 500 | 0.608 | 0.288 | 0.113 | 0.015 |
| 520 | 0.714 | 0.338 | 0.190 | 0.035 |
| 540 | 0.780 | 0.369 | 0.322 | 0.068 |
| 560 | 0.820 | 0.389 | 0.451 | 0.099 |
| 580 | 0.828 | 0.392 | 0.677 | 0.152 |
| 600 | 0.800 | 0.380 | 0.739 | 0.168 |
| 620 | 0.725 | 0.348 | 0.786 | 0.182 |
| 640 | 0.619 | 0.295 | 0.864 | 0.202 |
| 660 | 0.478 | 0.227 | 0.408 | 0.092 |
| 680 | 0.380 | 0.180 | 0.093 | 0.013 |
| 700 | 0.309 | 0.145 | 0.027 | 0.000 |

Table 8. Light Absorption of Reactive Dye Solutions

| Wave Length in Nanometer (nm) | Light Absorption of Reactive Dye Solutions* | | | |
|-------------------------------------|---|-------|--------------------------|-------|
| | Water | | DMF | |
| | Dye Concentration (g/l.) | | Dye Concentration (g/l.) | |
| | 0.100 | 0.050 | 0.050 | 0.010 |
| 400 | 0.173 | 0.079 | 0.069 | 0.008 |
| 420 | 0.200 | 0.093 | 0.086 | 0.009 |
| 440 | 0.225 | 0.104 | 0.109 | 0.016 |
| 460 | 0.228 | 0.106 | 0.128 | 0.021 |
| 480 | 0.247 | 0.116 | 0.145 | 0.024 |
| 500 | 0.380 | 0.183 | 0.164 | 0.028 |
| 520 | 0.636 | 0.307 | 0.230 | 0.042 |
| 540 | 0.950 | 0.460 | 0.350 | 0.068 |
| 560 | 1.320 | 0.636 | 0.492 | 0.100 |
| 580 | 1.530 | 0.744 | 0.656 | 0.135 |
| 600 | 1.700 | 0.797 | 0.682 | 0.141 |
| 620 | 1.430 | 0.705 | 0.732 | 0.155 |
| 640 | 0.830 | 0.408 | 0.530 | 0.116 |
| 660 | 0.328 | 0.160 | 0.200 | 0.042 |
| 680 | 0.122 | 0.059 | 0.063 | 0.008 |
| 700 | 0.058 | 0.025 | 0.028 | 0.000 |

Table 9. Light Absorption and Dye Concentration in Solutions

| Dye Concentration (g/l.) | Light Absorption of Dye Solutions* | | | |
|--------------------------------|------------------------------------|------------------------|--------------------------|------------------------|
| | Disperse Dye | | Reactive Dye | |
| | in Water (MWL 575 nm) | in DMF (MWL 640 nm) | in Water (MWL 600 nm) | in DMF (MWL 620 nm) |
| 0.010 | - | 0.213 | - | 0.165 |
| 0.020 | 0.083 | 0.360 | 0.165 | 0.322 |
| 0.050 | 0.393 | 0.880 | 0.797 | 0.730 |
| 0.080 | 0.628 | 1.390 | 1.280 | 1.140 |
| 0.100 | 0.830 | 1.750 | 1.700 | 1.470 |

MWL = Maximum Light Absorption Wave Length

* = The Reference Cell is the Pure Solvent

APPENDIX D

RESULTS OF EXPERIMENTS

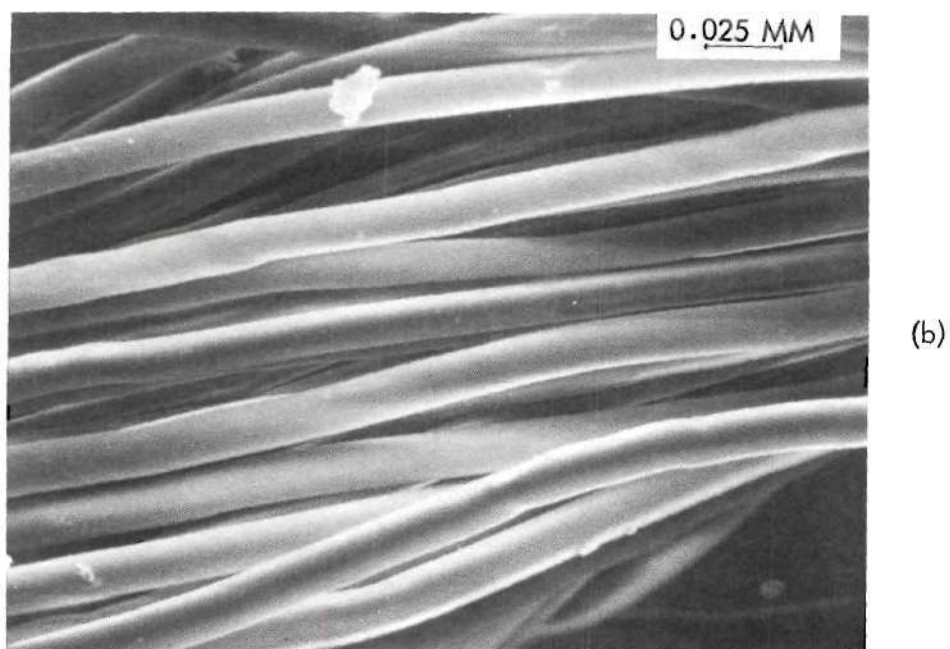
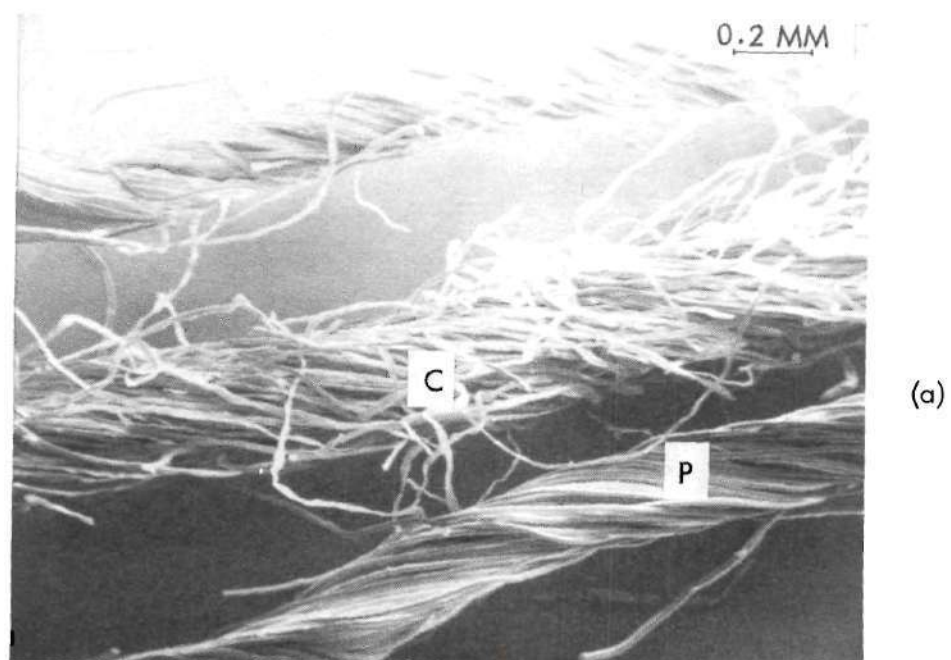


Figure 16. (a) Untreated Yarns (P = Polyester, C = Cotton)
(b) Untreated Polyester Fibers

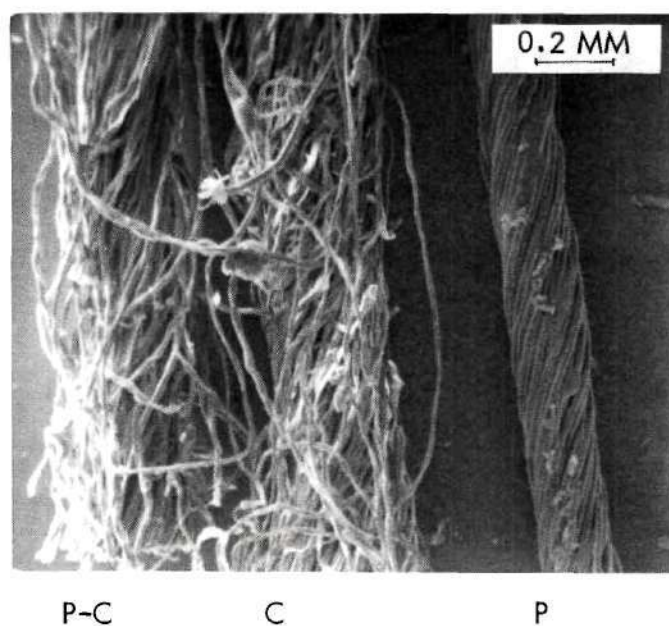


Figure 17. General View of HT-Steamed Yarns at 220 deg. C
(P = Polyester, C = Cotton, P-C = Polyester-Cotton)

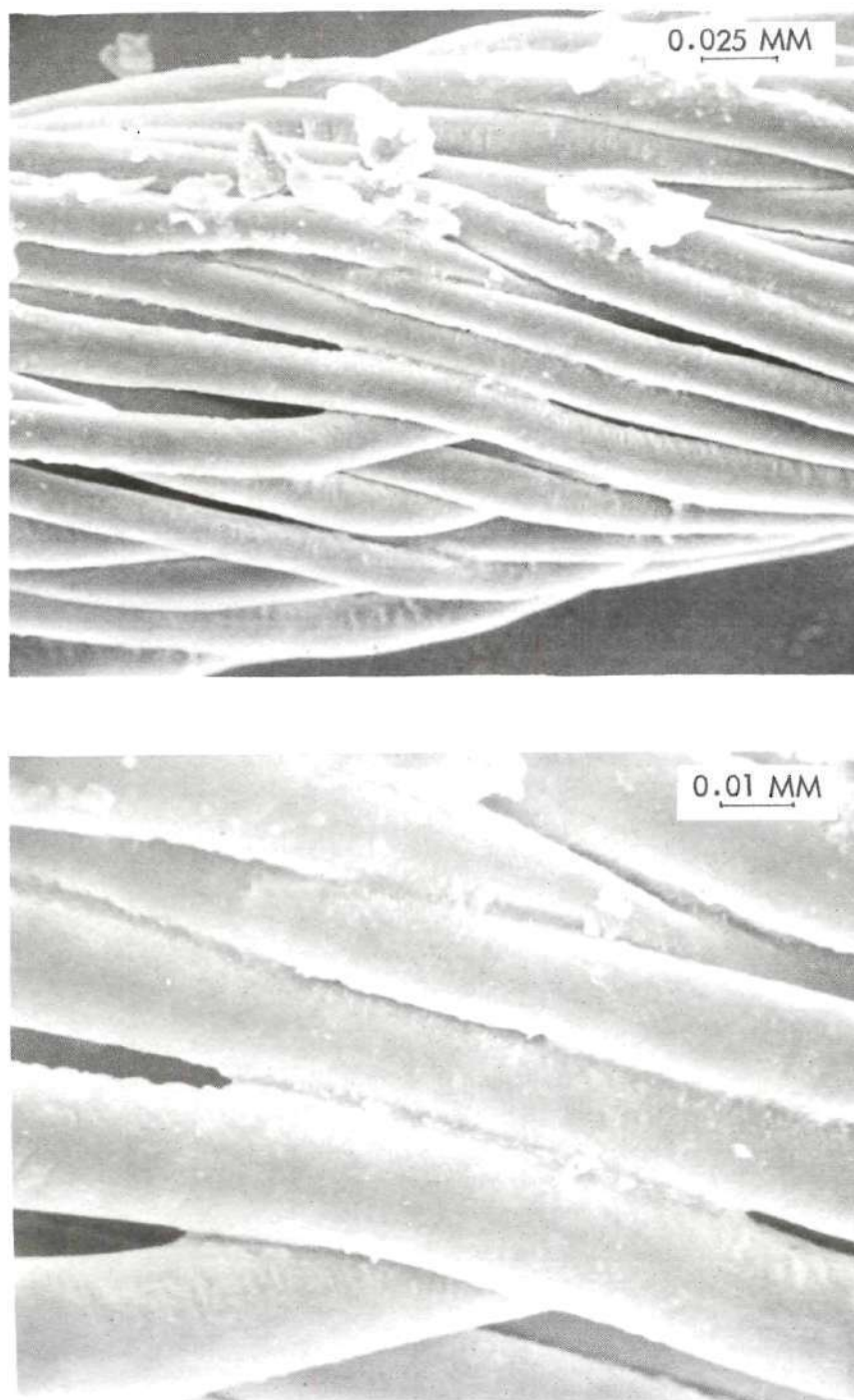


Figure 18. Polyester Fiber Fusion in a Polyester Yarn that has been HT-Steamed at 220 deg. C

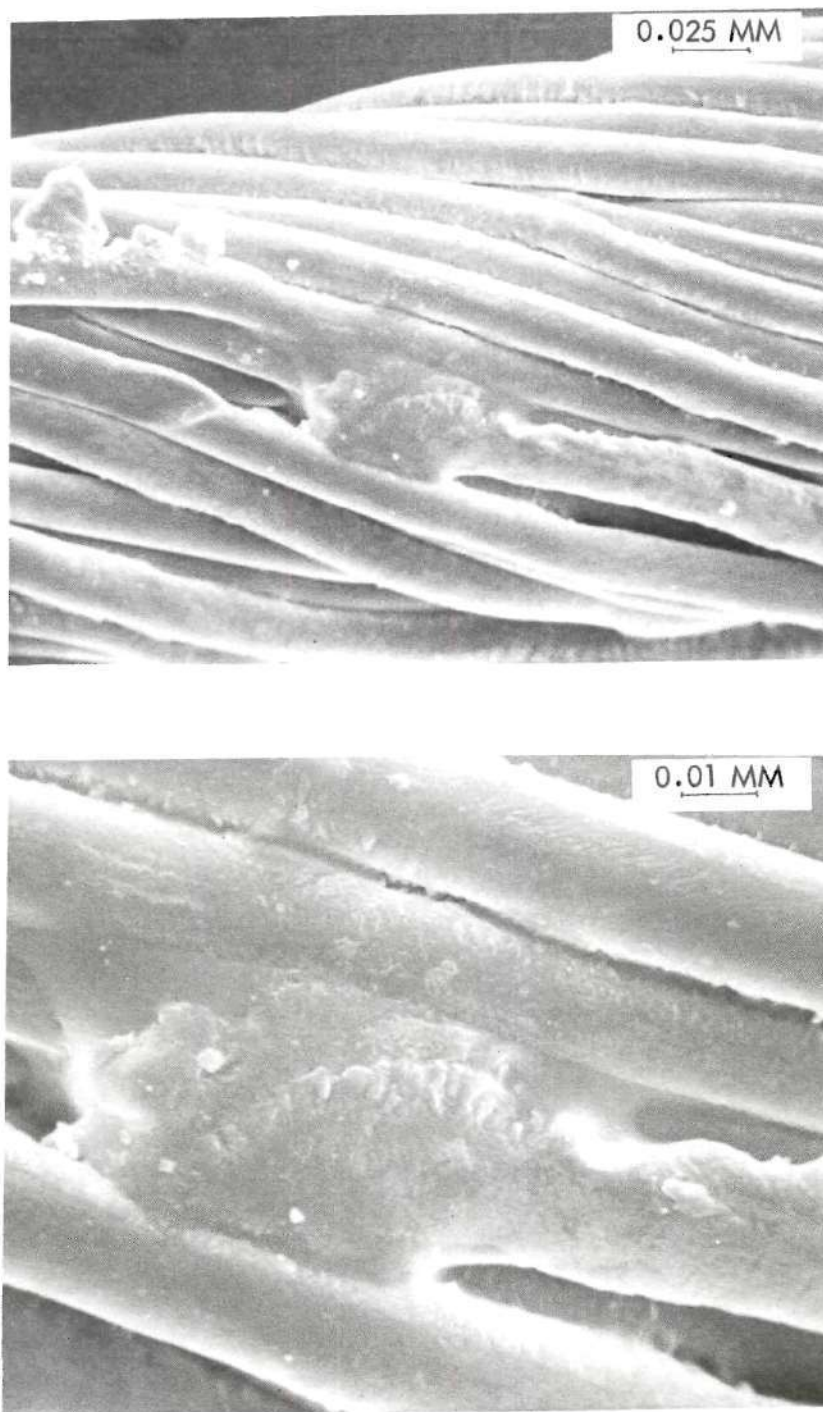


Figure 19. Polyester Fiber Fusion in the Polyester Yarn Due to Steaming at 220 deg. C

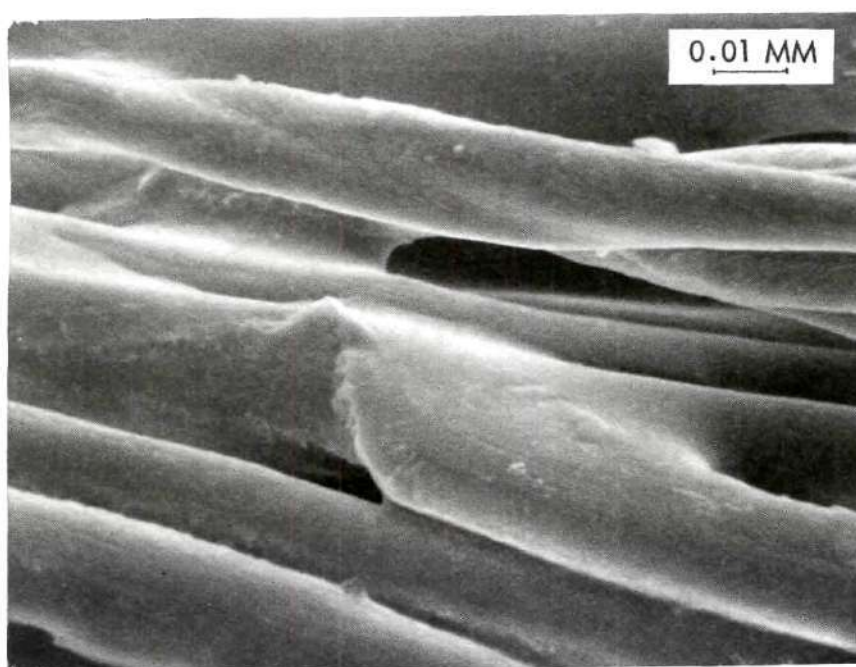
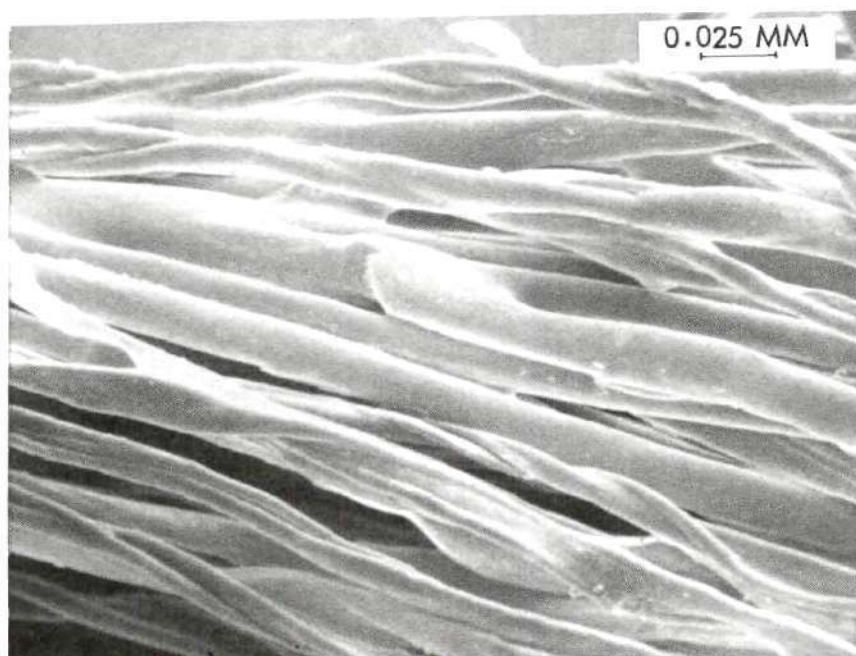
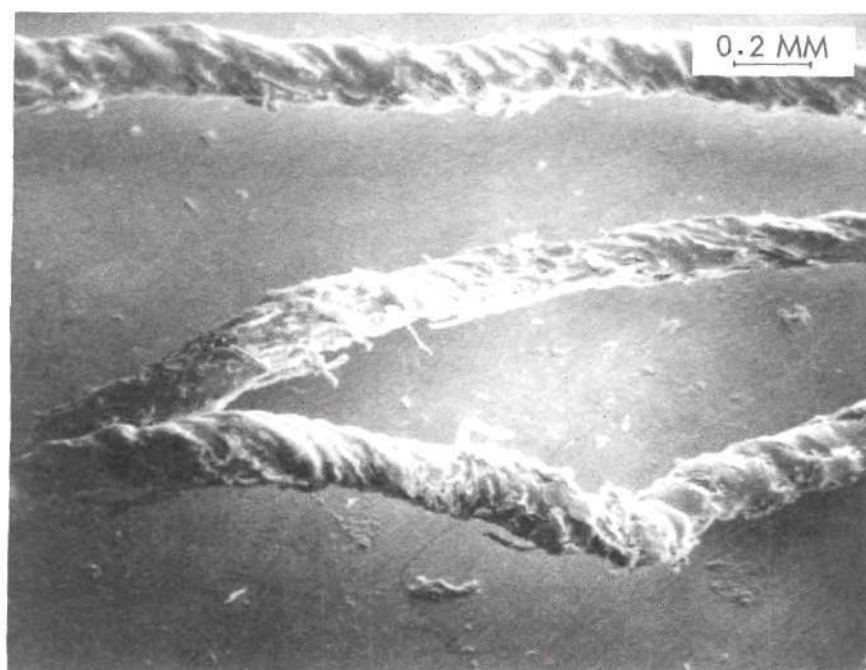
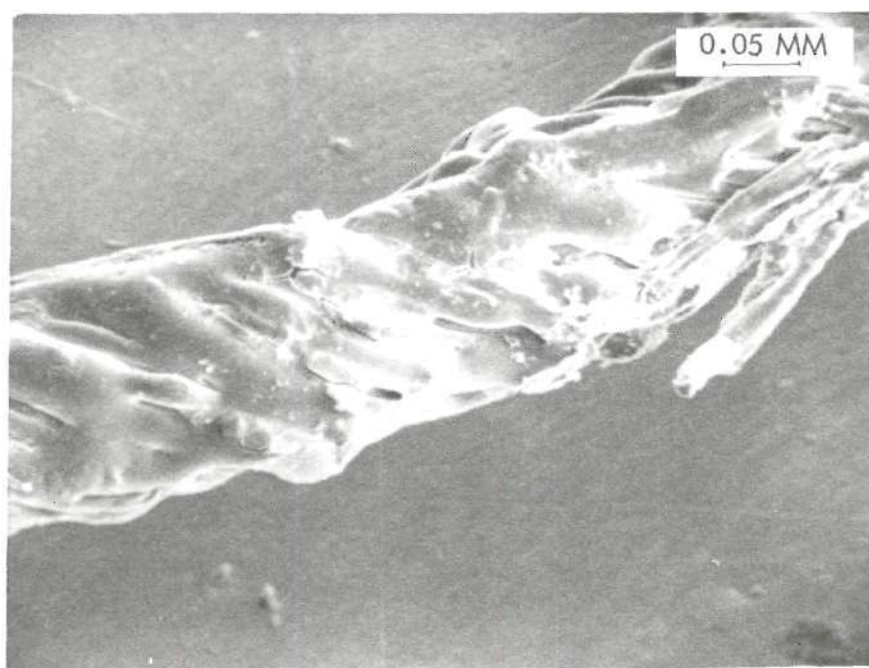


Figure 20. Polyester Fiber Fusion in the Polyester-Cotton Blended Yarn Due to Steaming at 220 deg. C



(a)



(b)

Figure 21. (a) General View of Polyester Yarn Broken Ends Due to HT-Steamming at 220 deg. C
(b) Polyester Fiber Partial Melting at the Yarn Periphery

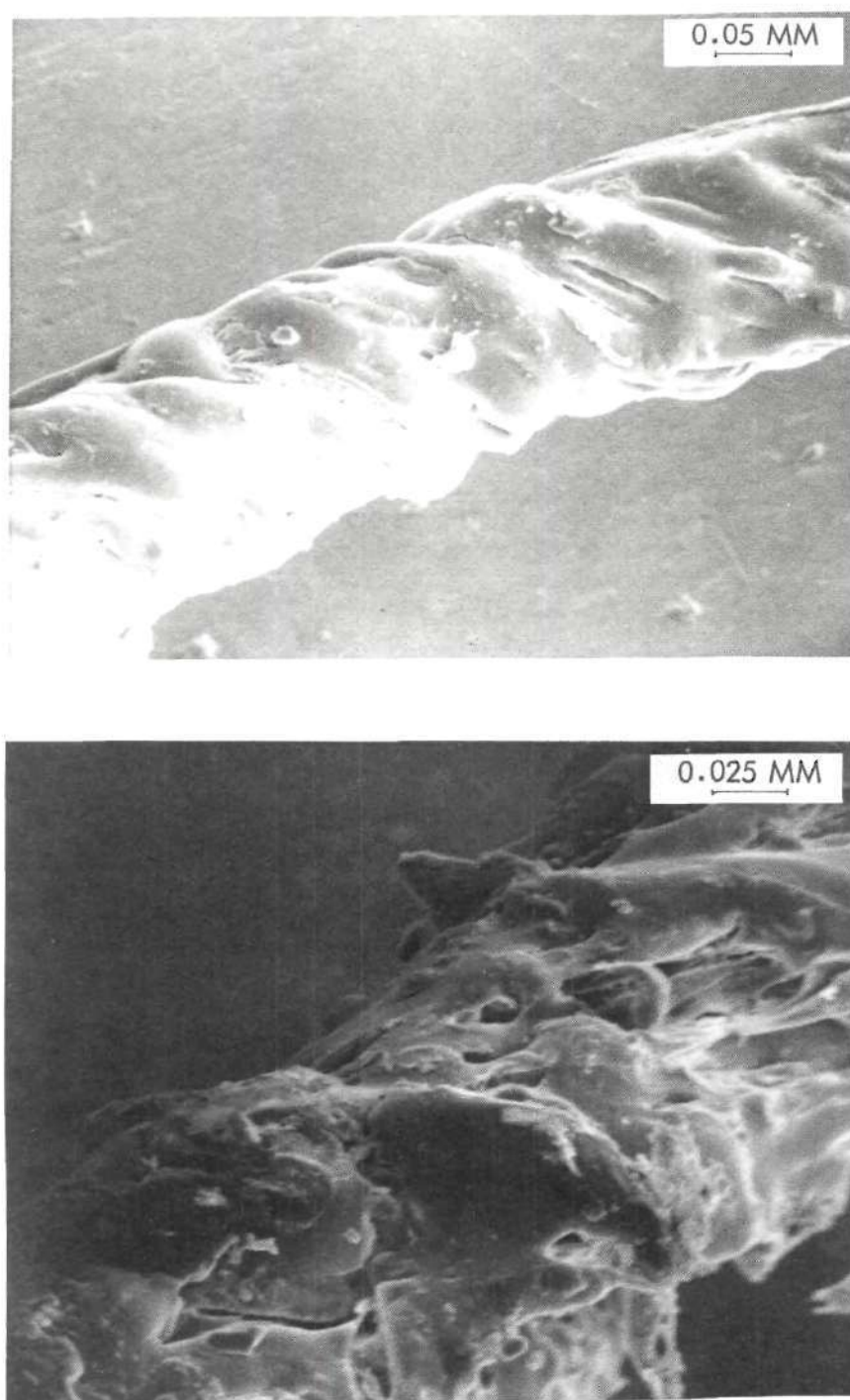
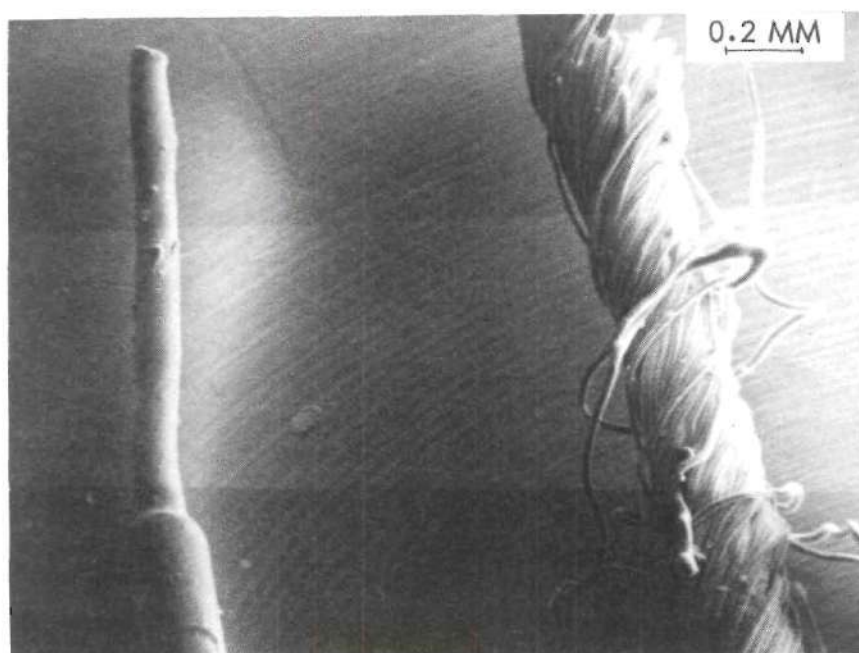


Figure 22. The Polyester Fiber Partial Melting at the Yarn Periphery



(a)



(b)

Figure 23. (a) Neck Formation in the Polyester Yarn Caused by HT-Steamming at 220 deg. C and Comparison to an Untreated Yarn
(b) Neck Cross Sectional View and Polyester Fibers in the Yarn Cavities

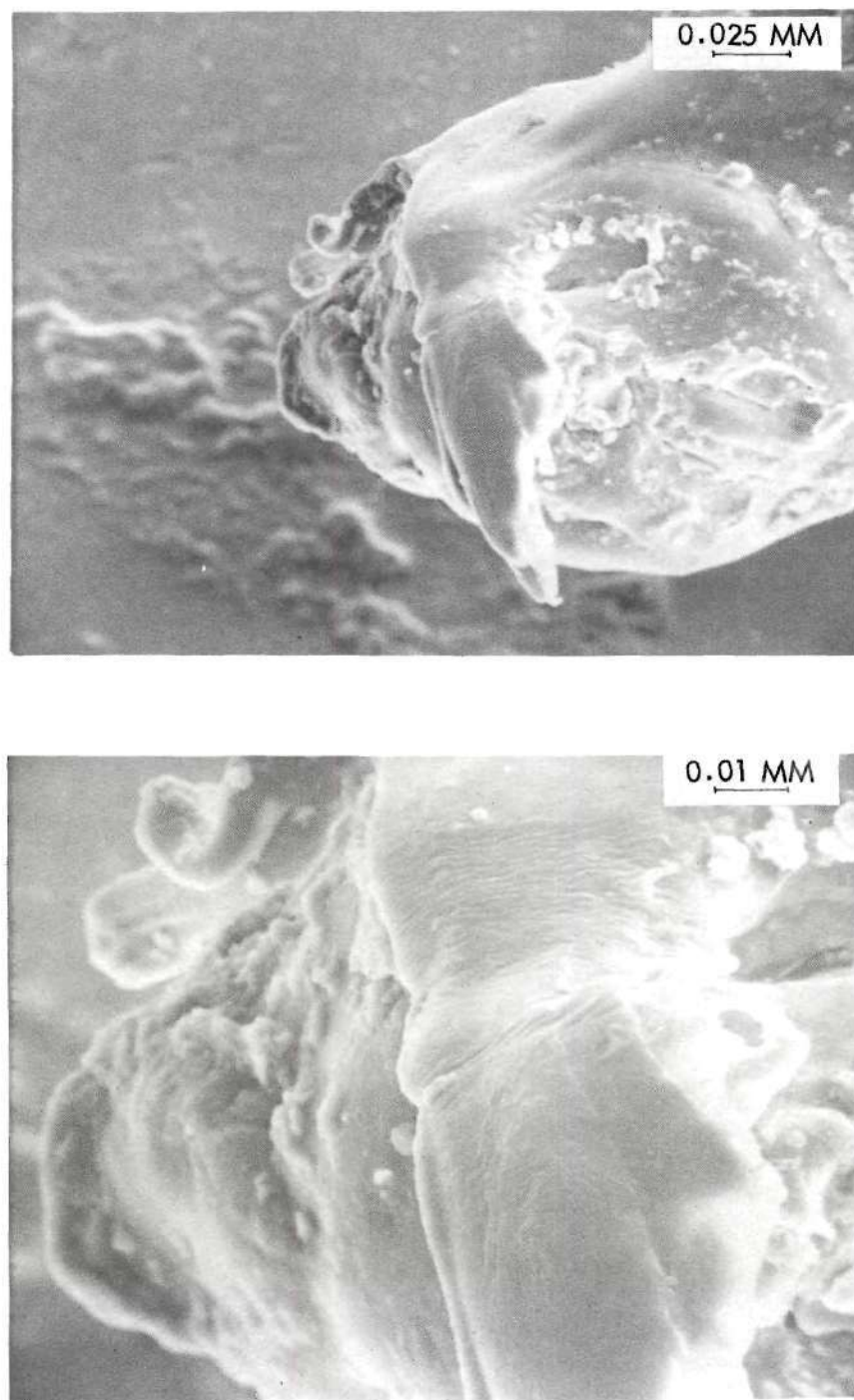
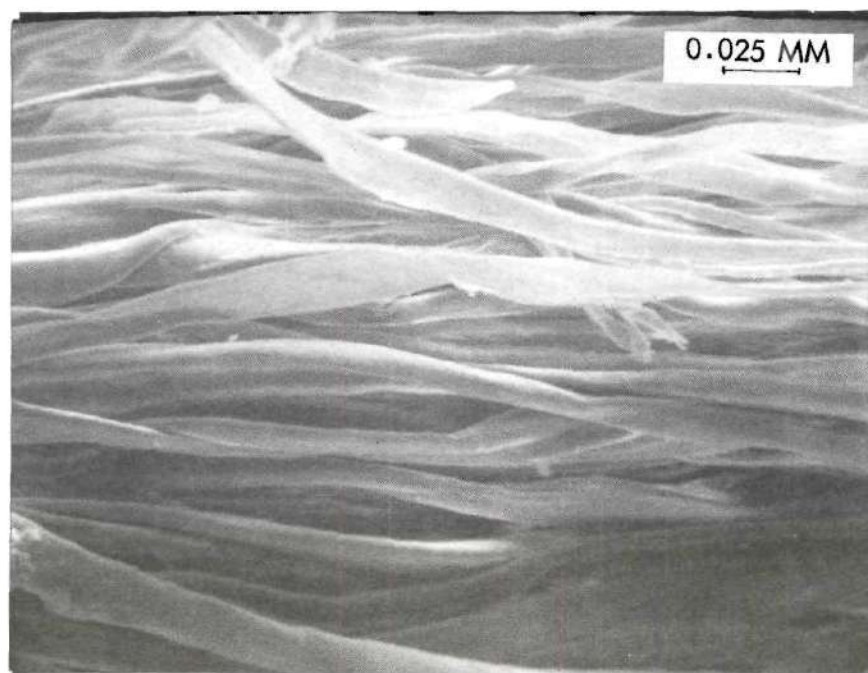
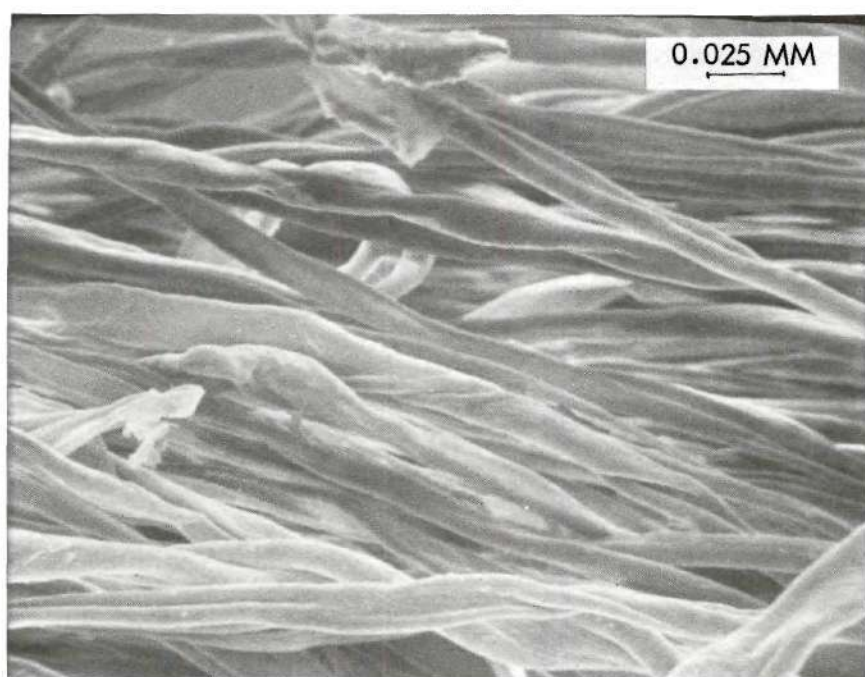


Figure 24. Neck Cross Sectional View

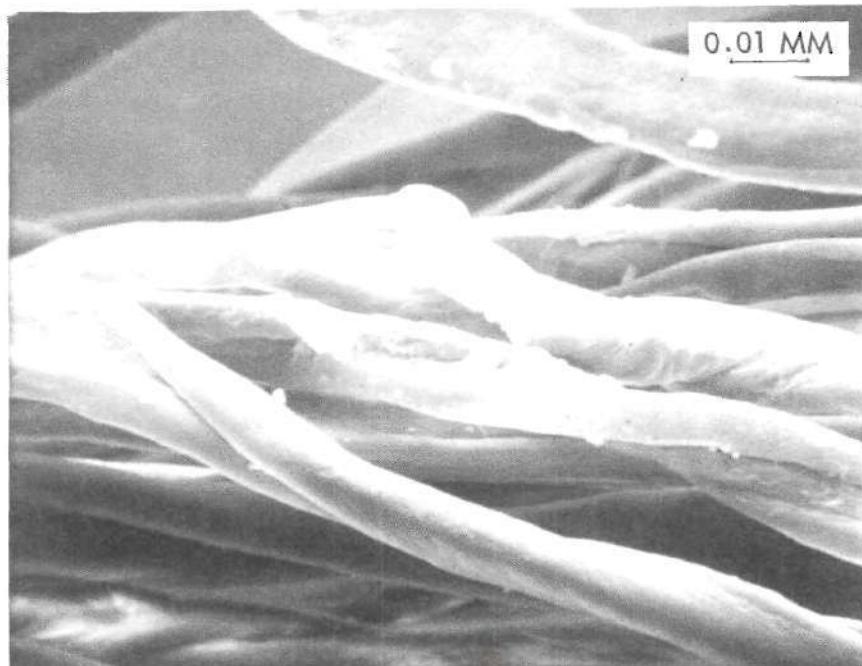


(a)

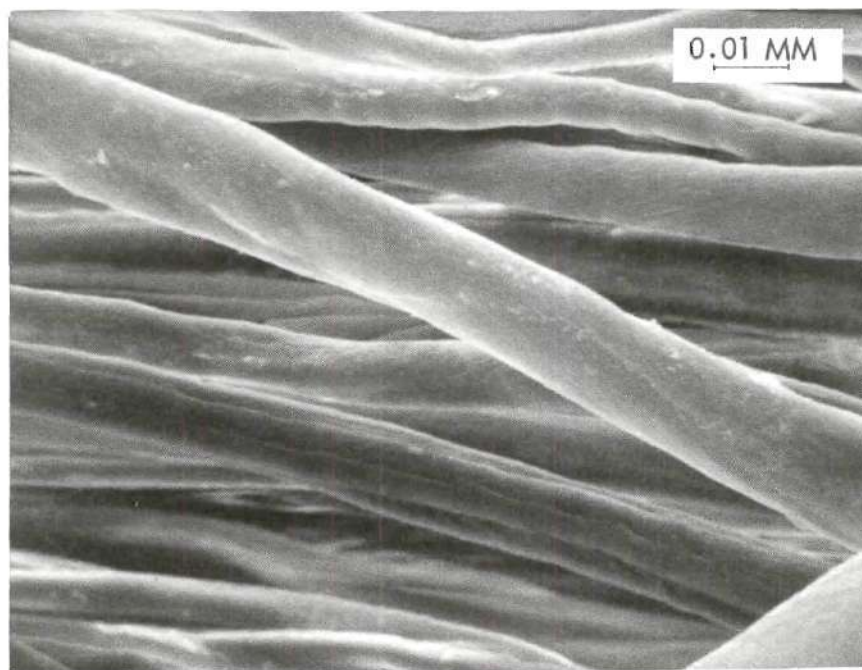


(b)

Figure 25. (a) Cotton Fibers prior to HT-Steaming
(b) HT-Steamed Cotton Fibers



(a)



(b)

Figure 26. (a) Untreated Cotton Fibers
(b) Steamed Cotton Fibers

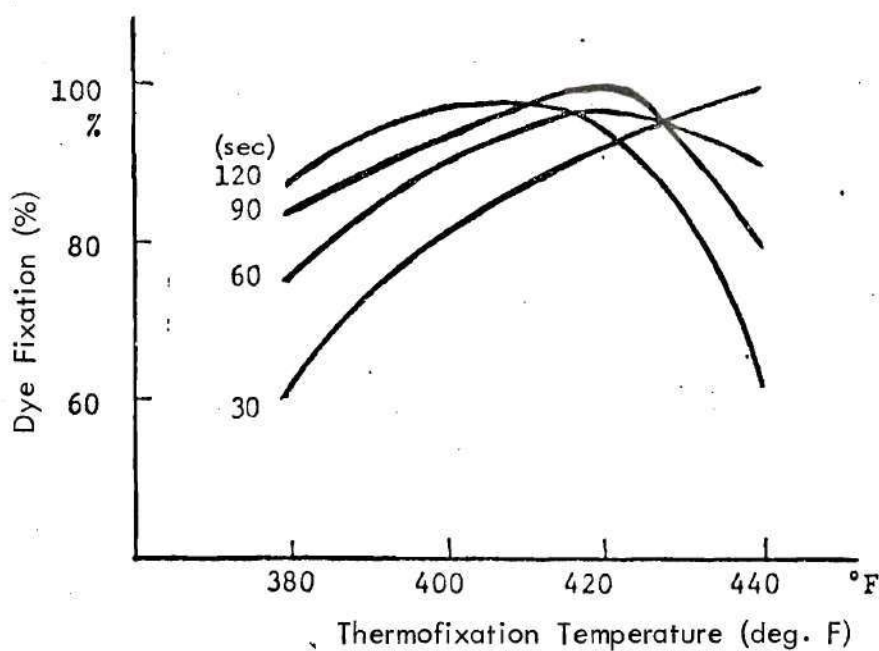
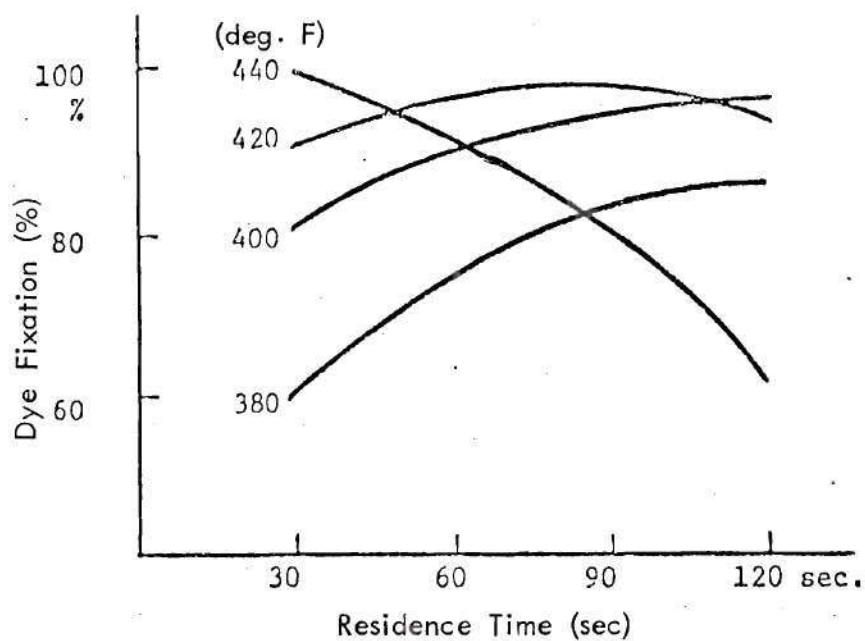
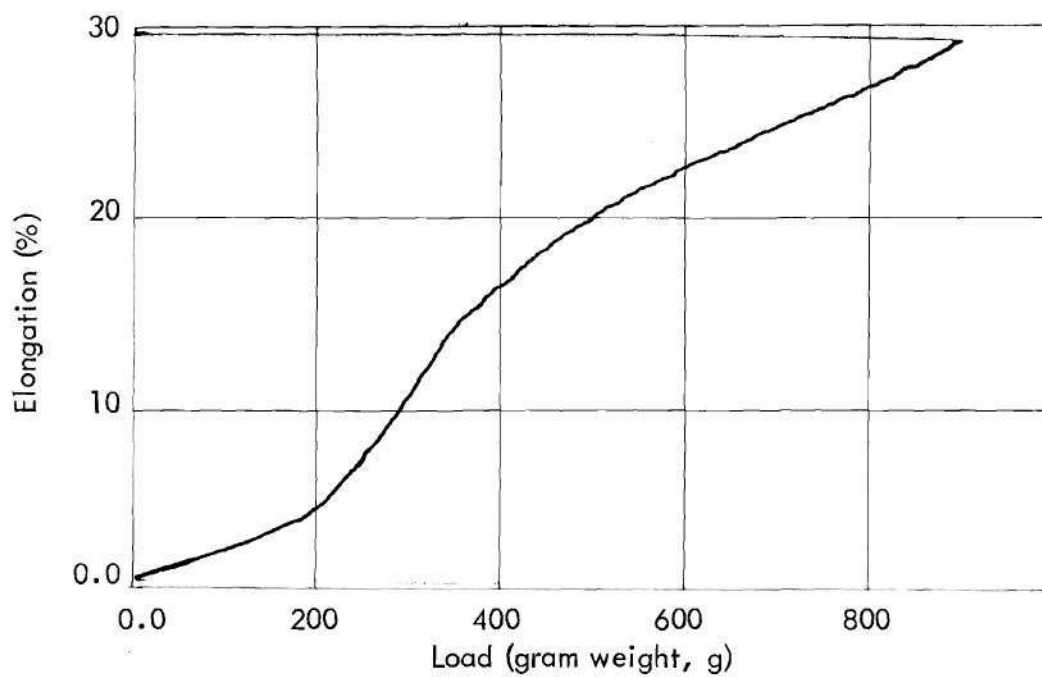
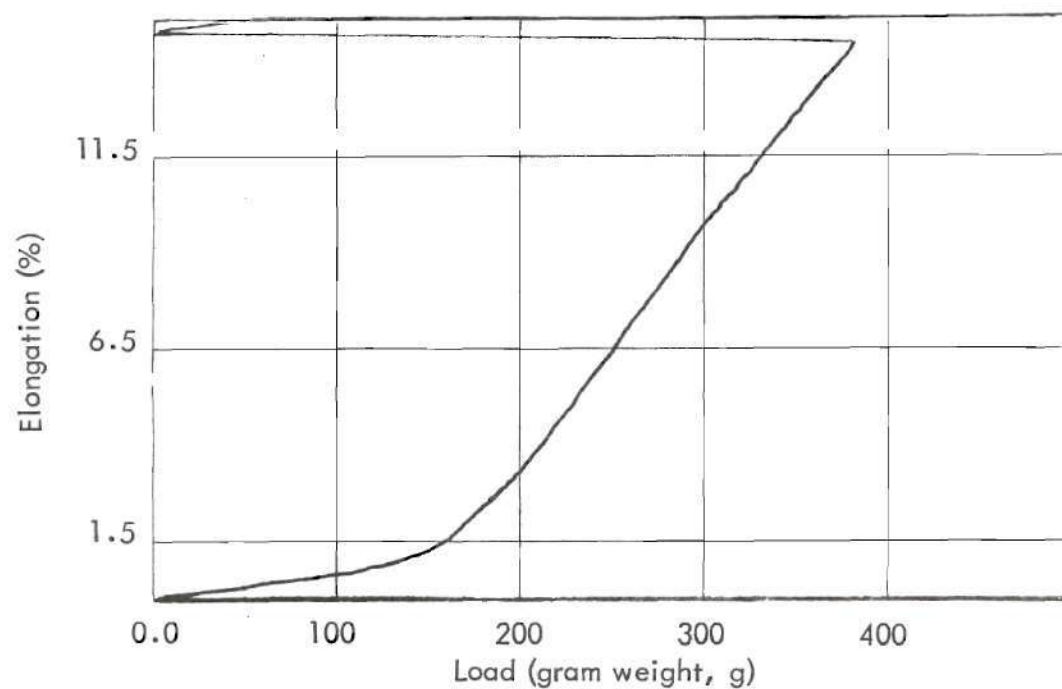


Figure 27. The Disperse Dye (Resolin Blue FBL, 50% Paste) Thermofixation Data
[Data is provided by the dye manufacture (65)]



Constant Rate of Extension = 12.7 cm/min (5 in./min)
Gauge Length = 25.4 cm (10 in.)

Figure 28. Untreated Polyester Yarn Load-Elongation Curve



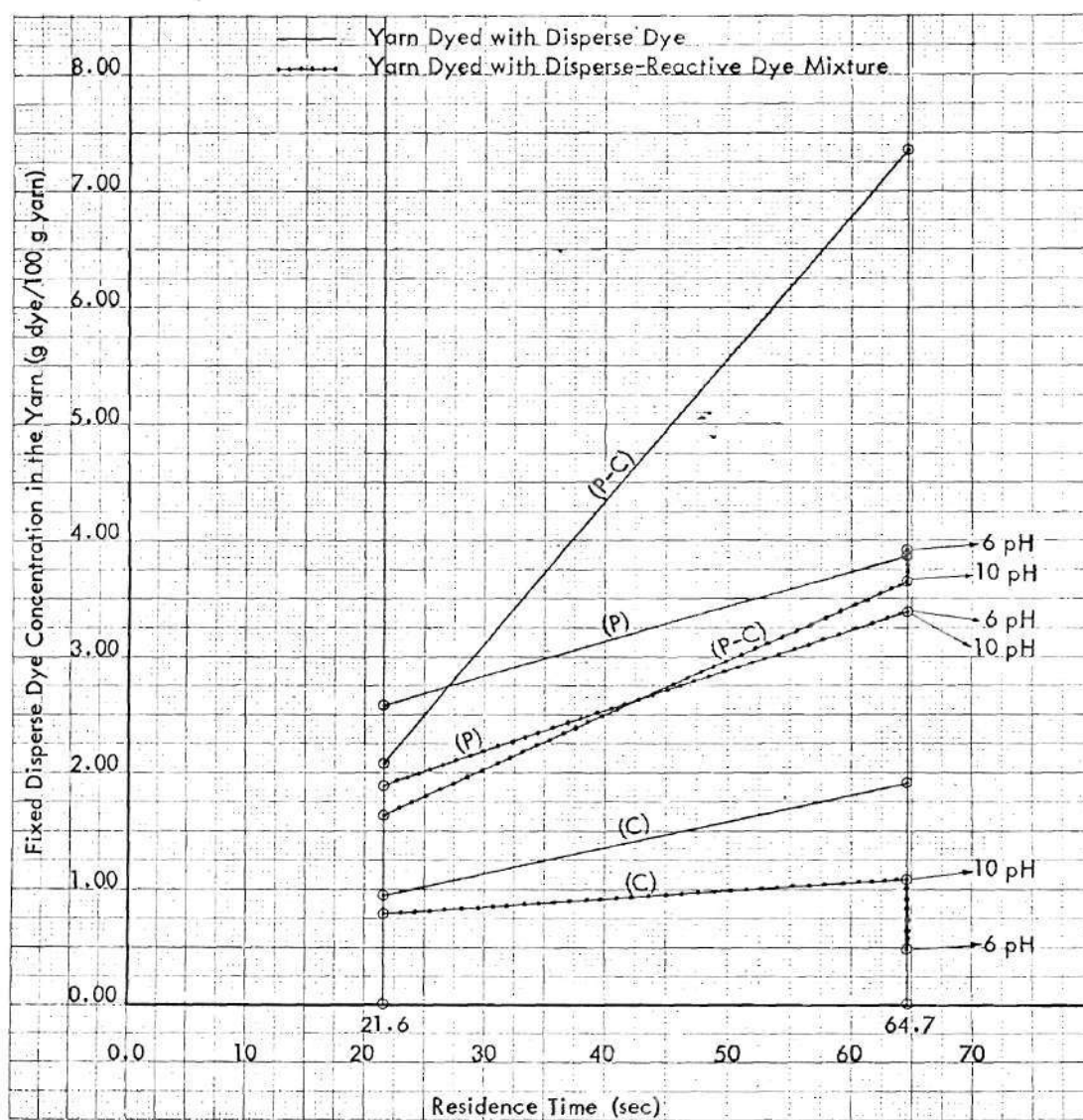
Constant Rate of Extention = 12.7 cm/min (5 in./min)

Gauge Length = 25.4 cm (10 in.)

Steaming Temperature = 220 deg. C

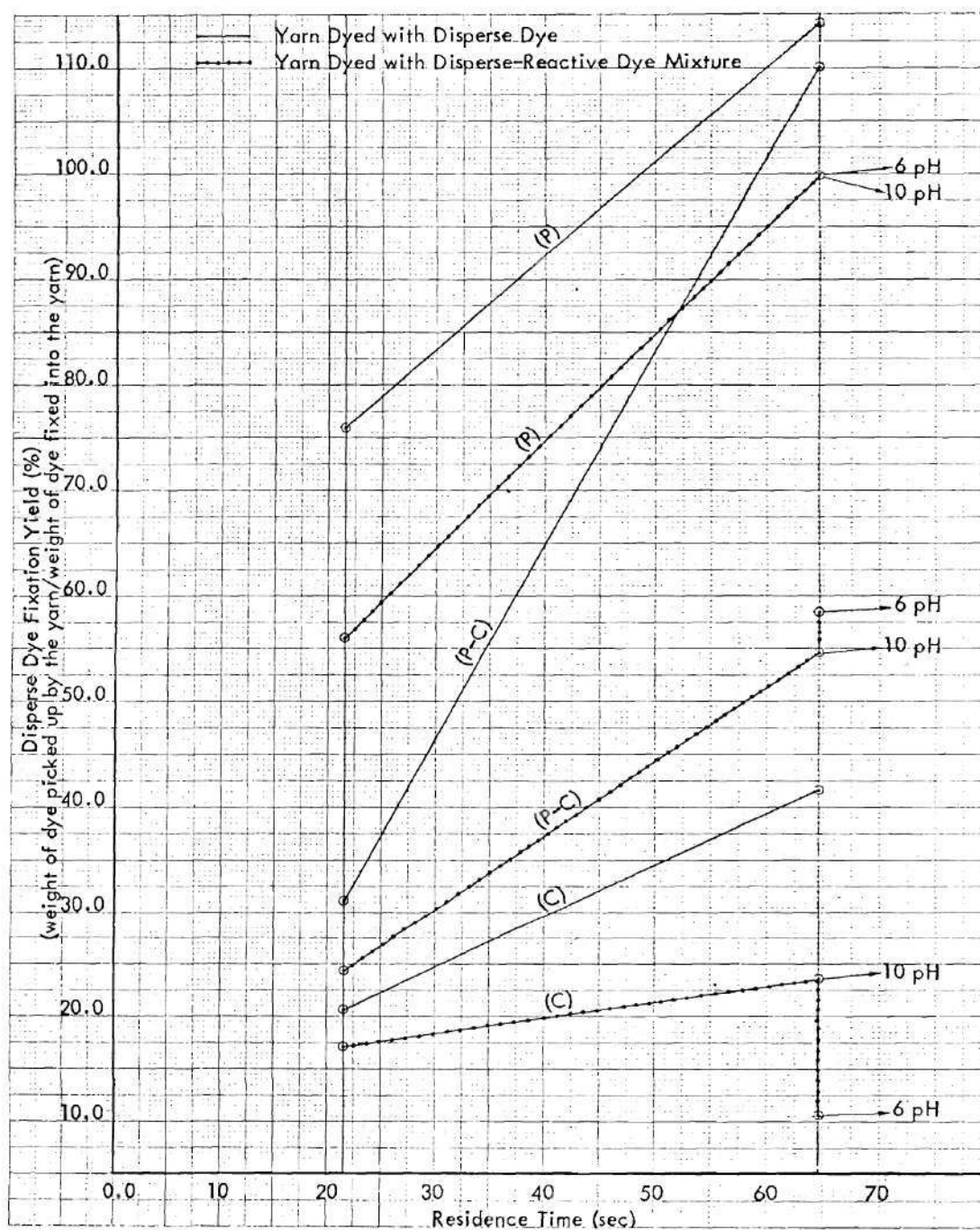
Residence Time = 2 min

Figure 29. HT-Steamed Polyester Yarn Load-Elongation Curve



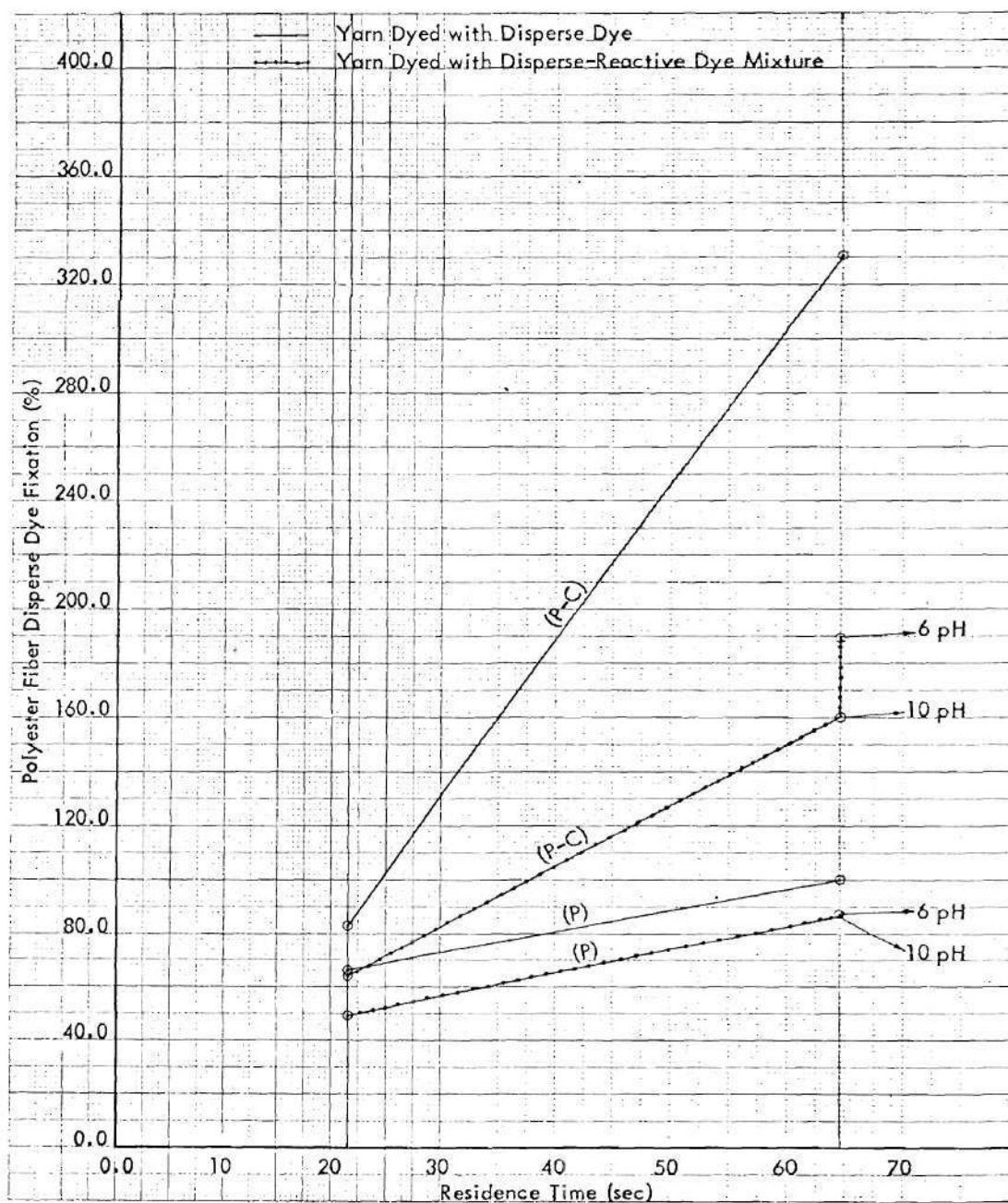
(P) = 100% Polyester Yarn
 (C) = 100% Cotton Yarn
 (P-C) = 50%-50% Polyester-Cotton Yarn

Figure 30. HT-Steam Disperse Dye Fixation
 [Data is from Table 10 in Appendix D]



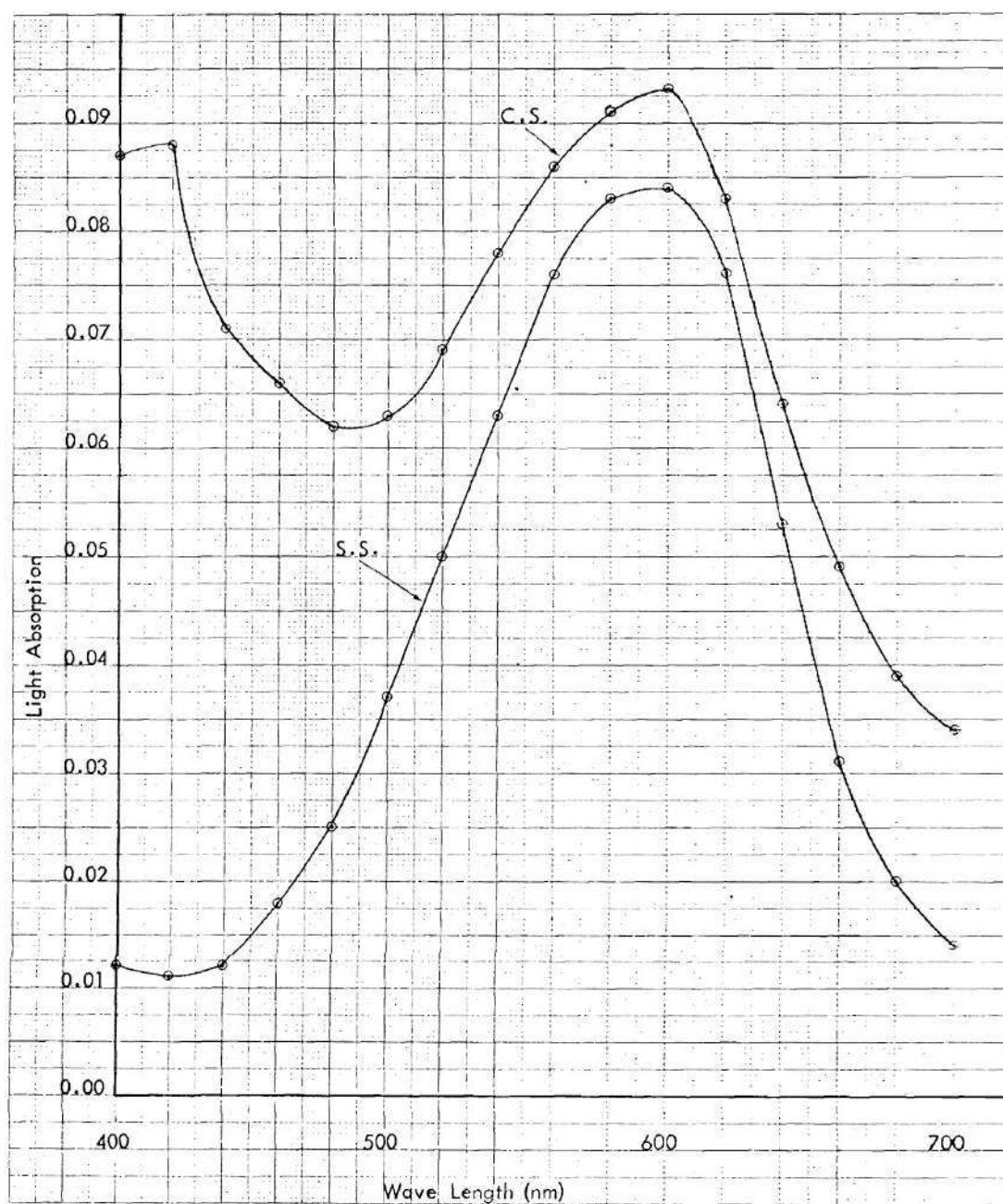
(P) = 100% Polyester Yarn
 (C) = 100% Cotton Yarn
 (P-C) = 50%-50% Polyester-Cotton Yarn

Figure 31. HT-Steam Disperse Dye Fixation Yield
 [Data is from Table 11 in Appendix D]



(P) = 100% Polyester Yarn
(P-C) = 50%-50% Polyester-Cotton Yarn

Figure 32. Polyester Fiber Disperse Dye Fixation in the Polyester Yarn and Blended Yarn [Data is from Table 12 in Appendix D]



C.S. = Condensed Steam Solution

S.S. = Simulated Dye Solution

Figure 33. Condensed Steam Solution and Simulated Dye Solution Spectra
[Data is from Table 13 in Appendix D]

Table 10. HT-Steaming Disperse Dye Fixation

| Padding Liquor Composition* | Residence Time (sec) | Disperse Dye Fixation (g dye/100 g yarn) | | |
|--------------------------------|----------------------------|--|--------------------------------------|-------------|
| | | P (100%) | Yarn Composition P-C (50%-50%) | C (100%) |
| D (pH 10) | 64.7 | 3.873 | 7.365 | 1.919 |
| | 21.6 | 2.574 | 2.081 | 0.949 |
| D + R (pH 10) | 64.7 | 3.386 | 3.650 | 1.083 |
| | 21.6 | 1.899 | 1.637 | 0.794 |
| D + R (pH 6) | 64.7 | 3.384 | 3.915 | 0.488 |
| | 21.6 | - | - | - |

* = See Chapter III for further Informations

P = Polyester

C = Cotton

D = Disperse Dye

R = Reactive Dye

Table 11. Disperse Dye Fixation Yield**

| Padding Liquor Composition* | Residence Time (sec) | Disperse Dye Fixation Yield (%) | | |
|--------------------------------|----------------------------|---------------------------------|--------------------------------------|-------------|
| | | P (100%) | Yarn Composition P-C (50%-50%) | C (100%) |
| D (pH 10) | 64.7 | 114.2 | 110.0 | 41.64 |
| | 21.6 | 75.90 | 31.08 | 20.59 |
| D + R (pH 10) | 64.7 | 99.84 | 54.51 | 23.50 |
| | 21.6 | 56.00 | 24.45 | 17.23 |
| D + R (pH 6) | 64.7 | 99.79 | 58.47 | 10.59 |
| | 21.6 | - | - | - |

* = See Chapter II for further Informations

** = Weight of Dye Fixed/Weight of Dye Picked Up (per unit weight of yarn)

P = Polyester

C = Cotton

D = Disperse Dye

R = Reactive Dye

Table 12. Polyester Fiber Disperse Dye Fixation in the Polyester Yarn and Blended Yarn**

| Padding Liquor Composition* | Residence Time (sec) | Polyester Fiber Disperse Dye Fixation (%) | |
|--------------------------------|----------------------------|---|--------------|
| | | Polyester Yarn | Blended Yarn |
| D (pH 10) | 64.7 | 100.0 | 330.8 |
| | 21.6 | 66.46 | 82.96 |
| D + R (pH 10) | 64.7 | 87.43 | 160.5 |
| | 21.6 | 49.03 | 64.03 |
| D + R (pH 6) | 64.7 | 87.37 | 189.6 |
| | 21.6 | - | - |

* = See Chapter II for further Information

** = Estimation method is described in Chapter IV

P = Polyester

C = Cotton

D = Disperse Dye

R = Reactive Dye

Table 13. Condensed Steam Solution and Simulated Dye Solution Spectra

| Wave Length (nm) | Light Absorption* | |
|---------------------|-----------------------------|---------------------------|
| | Condensed Steam Solution | Simulated Dye Solution |
| 400 | 0.087 | 0.012 |
| 420 | 0.088 | 0.011 |
| 440 | 0.071 | 0.012 |
| 460 | 0.066 | 0.018 |
| 480 | 0.062 | 0.025 |
| 500 | 0.063 | 0.037 |
| 520 | 0.069 | 0.050 |
| 540 | 0.078 | 0.063 |
| 560 | 0.086 | 0.076 |
| 580 | 0.091 | 0.083 |
| 600 | 0.093 | 0.084 |
| 620 | 0.083 | 0.076 |
| 640 | 0.064 | 0.053 |
| 660 | 0.049 | 0.031 |
| 680 | 0.039 | 0.020 |
| 700 | 0.034 | 0.014 |

* = Reference Solution is distilled water and the maximum light absorption wave length is 600 nm.

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